Mass Release of Chlorinated Solvents through Oil, Adsorbent, and Polyethylene Bagging at the Radioactive Waste Management Complex

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Idaho Completion Project

Bechtel BWXT Idaho, LLC

November 2003

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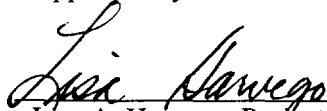Wayne Downs
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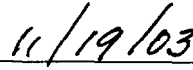Brigham Young University
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ICP/EXT-03-00057
Revision 0

Approved by

Lisa A. Harvego, Project Engineer   Date
Organic Contamination in the Vadose Zone

ABSTRACT

Drums buried at the Idaho National Engineering and Environmental Laboratory Radioactive Waste Management Complex contain radionuclides, cutting oil, and chlorinated solvents. These materials had been placed in steel barrels lined with high-density polyethylene bags before shipment to Idaho for emplacement. Many, if not all, of these drums are expected to have corroded to some degree in the years since burial, and there is interest in estimating the rate of release of solvents from the drums.

This work focuses on estimating effective diffusion coefficients and mass loss rates of four chlorinated solvents (carbon tetrachloride, 1,1,1-trichloroethane, trichloroethene, and perchloroethene) through cutting oil (Texaco Regal Oil), calcium silicate absorbent, and polyethylene bagging.

Activity coefficients were determined for the solvents in relation to one another and the oil. Results show insignificant molecular interaction among the solvents that would affect their diffusion.

Effective diffusion coefficients were estimated empirically and then confirmed by fitting experimental data generated gravimetrically for binary systems and by gas chromatography/mass spectrometry analysis for ternary systems with an applicable analytical solution for transient diffusion. The diffusion coefficient in the analytical expression was adjusted to match observed diffusive mass loss, measured gravimetrically. Effective diffusion coefficients for the four chlorinated solvents in oil were both estimated and observed to be within the range of 2.7×10^{-6} to 6.8×10^{-6} cm^2/second.

In an oil-and-calcium silicate matrix, mass loss of chlorinated solvent was observed to be slightly lower than, but within an order of magnitude, of that observed in the liquid/liquid mix.

To simulate solvent loss from buried drums, small aluminum canisters were packed with the solvents in an oil-and-calcium silicate matrix. Different diameter holes were drilled in the canisters to simulate various levels of corrosion. Mass loss from the canisters was scaled to match loss from 55-gal drums (without polyethylene bagging). The scaled time for solvent loss from the drums was estimated to be on the order of a few years.

The role of polyethylene bagging was evaluated by applying mole fraction concentrations of solvent mixes determined from the latest available information on drum contents to permeability estimates from Liekhus and Peterson (1995). Diffusion through polyethylene bagging was determined to be the limiting factor affecting escape from the drums by reducing the rate of escape from diffusion alone by another four orders of magnitude. Solvent escape was estimated to be accomplished from 35 to 65 years, depending upon drum and bagging integrity.

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TABLES

ACRONYMS

GC/MS	gas chromatography/mass spectrometry
INEEL	Idaho National Engineering and Environmental Laboratory
NRTL	nonrandom two-phase liquid
PCE	tetrachloroethene
SDA	Subsurface Disposal Area
TCA	1,1,1-trichloroethane
TCE	trichloroethene
TRO	Texaco Regal Oil
UNIFAC	universal functional activity coefficient
VOC	volatile organic compound

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1. INTRODUCTION

1.1 History

The production of chlorinated solvents began in the United States around 1906. Widespread use of chlorinated solvents began during World War II in the industrial effort to support the war and increased markedly during the next *3* decades. The subsequent disposal and concurrent contamination of the groundwater by these compounds went undetected for years. In the late sixties, Dr. Leslie L. Glasgow, chairman of the Louisiana Stream Control Commissioner of the U.S. Federal Water Pollution Control Administration, requested testing of the city of New Orleans drinking water because of numerous complaints from the city's citizens. Results of the study revealed "a wide variety of 'extractable' organic compounds" in New Orleans drinking water (Pankow and Cherry 1996).

As a result of this study and others like it, Congress enacted the Clean Water Act on October 18, 1972. This act was designed to regulate discharges into all navigable waters of the United States. At the time, the Clean Water Act did not deal with groundwater issues. In order to comply with the new regulations, many chemical manufacturers suggested that to properly dispose of chemical waste, one should "bury the [trichloroethene (TCE), tetrachloroethene (PCE), and 1,1,1-trichloroethane (TCA)] away from water supply or allow solvent to evaporate to the atmosphere at a safe distance from inhabited buildings" (Pankow and Cherry 1996). Unbeknownst to industry, a majority of the solvent would, in fact, quickly move through the vadose zone and to the water table, particularly in that of porous geology. Contamination of the groundwater continued through the early seventies.

After the development of computerized gas chromatography/mass spectrometry (GC/MS) analytical equipment in the early seventies, the U.S. Environmental Protection Agency filed a public report in 1974, which declared that 66 trace organic compounds (including carbon tetrachloride, TCA, TCE, and PCE) were found and identified in the Mississippi River (Pankow and Cherry 1996). This led to legislation of the Safe Drinking Water Act in 1974.

As analytical equipment sensitivity continued to improve, the evidence that chlorinated solvents were widespread groundwater contaminants was obvious. In 1976, the Toxic Substances Control Act was signed, establishing a regulatory framework for controlling the release of toxic substances to the environment. Shortly afterward, the Resource Conservation and Recovery Act was passed to address the issue of safe disposal of the huge quantities of solid and hazardous waste generated in the United States each year.

Reports of groundwater contamination by chlorinated solvents dramatically increased in the early eighties. The State of New Jersey reported in 1982 that 1,076 wells were contaminated with TCE and TCA. The reports of groundwater contamination continued throughout the eighties culminating in the passing of the Hazardous and Solid Waste Amendments Act in 1986. This act mandated the monitoring of groundwater and the vadose zone throughout the United States.

Since the late eighties, tremendous effort and finances have been directed toward remediation efforts at numerous sites throughout the world that are contaminated with a wide variety of dense nonaqueous-phase liquids, such as TCE, TCA, and carbon tetrachloride. Results from all of these sites

reveal that chlorinated solvents in the dense-nonaqueous-phase-liquid form tend to persist in the subsurface for long periods, even in the face of aggressive remediation efforts. Understanding the movement and fate of chlorinated solvents in groundwater has now advanced to a point where the major aspects of how chlorinated solvents move in the surface and subsurface are reasonably well understood. Transport properties of chlorinated solvents in groundwater, such as solubility, diffusivity, and partitioning coefficients, are readily available in numerous textbooks, databases, and research journals (Watts **1997).**

1.2   Past Disposal Practices

Before legislation, there was no pressure for industry to use other than the most simple and economical methods for disposing of waste chemicals. Disposal frequently involved storing hazardous waste on the work site or sending it along with nonhazardous materials to a landfill. Other methods of disposal include soil spreading, shallow pits, and midnight dumping at a different site. During this period, these means of disposal were not perceived as being dangerous, as society had no comprehension of the potential adverse health effects or of the persistent nature of hazardous waste (Watts **1997).**

Through the advancement of analytical methods and instrumentation, the problem of improper disposal itself has been identified and rectified; however, the results of poor practices of the past still remain. It has been reported by the National Academy of Sciences that up to 500 years will be required to see the full effects of improper chlorinated solvent disposal in the subsurface (Pankow and Cherry **1996).** Hazardous waste from old dumping areas continues to find its way into the subsurface. Some sources are unknown, but others are well documented. One such site that is the focus of this study is the Radioactive Waste Management Complex located at the Idaho National Engineering and Environmental Laboratory (INEEL) Site near Idaho Falls, Idaho.

1.3   Background

The Radioactive Waste Management Complex was used as a disposal site for waste solvents and oil from the Aqueous Waste Treatment Facility at the U.S. Department of Energy Rocky Flats Plant near Denver, Colorado. This liquid is classified as lathe coolant; used hydraulic, gearbox, and spindle oils; and degreasing agents used in the milling operations of radioactive materials (Downs and Hansen **1994).** The liquid waste was collected by pipeline into a common tank and processed by blending approximately **30** gal of liquid with **100** lb of calcium silicate or Portland cement in a continuous mixer to form a solidlike paste (solidification). The resulting solid material was placed in 55-gal barrels lined with high-density polyethylene bagging. It has been documented that approximately **9,680** drums, containing what has been coined by the INEEL as the Series **743** sludge, were buried in the pits and trenches at the Subsurface Disposal Area (SDA) at the Radioactive Waste Management Complex over a period of **4** years from **1966** to **1970** (Miller and Varvel **2001).** These Series **743** drums are reported to contain the following contaminants:

- **688,000** kg carbon tetrachloride

- **166,000** kg TCE

- **160,000** kg TCA

- **42,000** kg PCE

- 5,000 kg 1,1,2-trichloro-1,2,2-trifluoroethane (Freon **113).**

These five contaminants in the Series 743 drums equal a total of 1,061,000 kg.

The presence of such large volumes of toxic chemicals in the subsurface presents a significant threat to the environment. However, because of the presence of radioactive materials in the barrels, the threat of radioactive contamination by excavation outweighs the threat of groundwater contamination. In an attempt to remediate the problem, the INEEL has resorted to an extensive network of soil vapor extraction wells to extract the various solvents escaping from the buried drums where drum integrity has been compromised through corrosion.

As part of an effort to expedite the remediation process, the Environmental Restoration group at the INEEL is interested in developing a model to estimate the quantity of waste remaining in the drums. The model will provide valuable information to help determine future hazardous waste management strategies. The uniqueness of the problem facing the INEEL is to understand how the solvents migrate in relation to one another through a medium composed of nonaqueous liquid and an absorbent.

1.4 Research Objectives

The following are the objectives of this research:

- Determine the degree of molecular interactions between the chlorinated solvents and the Texaco Regal Oil (TRO) through thermodynamic analysis (activity coefficients)

- Find and use empirical methods to estimate effective diffusion coefficients, then confirm those values by fitting experimental data generated by gravimetric (binary) and GC/MS (ternary) analysis with the analytical solution for transient diffusion

- Evaluate the effect of the calcium silicate matrix on the evaporative loss of chlorinated solvents in TRO

- Evaluate the effect on the rate of mass loss of chlorinated solvent in TRO with calcium silicate matrix in sealed canisters with a single-drilled-hole size (e.g., 1/4 in., 1/8 in., or 1/16 in.).

As part of the effort to create a model to estimate the quantities of waste left in the drums, it is necessary to come to an understanding of the complex interactions of the various components and how these interactions affect the rates of diffusion. Once these issues are addressed, the process of creating a programmed model to estimate the amount of chlorinated solvents left at the SDA will aid in future management and remediation strategies.

2. LITERATURE REVIEW

2.1 Introduction

Throughout scientific literature, diffusion coefficients are most often discussed in terms of binary pair systems, whether they are in gas or liquid phase. In the case of gases, the theory describing binary diffusion at low to moderate temperatures (environmental conditions) has been researched extensively (Reid, Prausnitz, and Poling 1987). Diffusion coefficients under these conditions are almost entirely independent of composition and inversely proportional to pressure, and they vary with the absolute temperature to around the 1.5 power (Taylor and Krishna 1993). Two methods based upon the ideal gas law, the Wilke-Lee and Fuller methods, have been found to accurately predict most binary gas diffusion coefficients to within 5 to 10% of experimental values (Reid, Prausnitz, and Poling 1987).

The use of the ideal gas law in calculating gas diffusivity implies an ideal gas. An ideal gas is one in which no intermolecular interactions exist and there are no excluded volumes for the molecules. Because of the low density of molecules at ambient conditions, the average molecule is a significant distance from its neighbor. Consequently, these molecules exert negligible forces on each other, and gas behavior can be accurately estimated using the ideal gas law.

Binary liquid diffusion coefficients are more difficult to define than those of gases. Since molecules in liquids are densely packed and strongly affected by force fields of neighboring molecules, the interactions between molecules are much more complex.

2.2 Activity Coefficients

The definition of an ideal liquid is different from that of an ideal gas. Since intermolecular interactions do occur, they cannot be neglected. An ideal liquid is best defined in terms of a binary pair consisting of A and B components. In an ideal solution, the average A-B interactions in the mixture are the same as the average A-A and B-B interactions (Valsaraj 1995). These interactions are primarily based upon the potential of a molecule to form hydrogen bonds (Henley and Seader 1981).

A classification system designed by Ewell, Harrison, and Berg considers the four chlorinated solvents and the TRO oil contained in the liquid fraction of Series 743 sludge as either Class IV or Class V molecules. According to their data, any combination of Class IV and V molecules results in solutions where no hydrogen bonding is involved (Henley and Seader 1981). The resulting binaries are described as being either a quasi-ideal solution with minor positive deviations or simply an ideal solution.

A term commonly used in chemical engineering to describe deviations from ideality in solutions is a nondimensional quantity called the activity coefficient (y). In the case of an ideal solution, the activity coefficient is unity. An activity coefficient greater than one in terms of vapor-liquid equilibria can be described as a high-energy liquid mixture that must donate excess energy to the lower energy vapor phase to achieve equilibrium. This excess energy is transferred by movement of the energy-containing molecules to the vapor phase resulting in higher pressures compared to an ideal case. Activity coefficients less than one imply a low-energy liquid mixture that retains its energy resulting in low vapor pressures to attain equilibrium. For purposes of this study, it is best to view this energy transfer in terms of escapability (i.e., the escaping power of each component in the mix according to its level of energy). Therefore, activity coefficients are used to indicate whether cumulative interactions are occurring in a mixture and, if so, which direction these shifts in energy occur. It is important to note that activity coefficients are functions of temperature, pressure, and concentration. For a detailed discussion regarding the derivation and subsequent definition of activity coefficients, refer to Appendix A.

There are both empirical and semitheoretical equations available to estimate activity coefficients for liquid binary pairs. A commonly used method for calculating activity coefficients, whether they be based upon measured data or a theoretical estimates, is the nonrandom two-phase liquid (NRTL) equation shown in Equation 2-1 (Henley and Seader 1981):

$$\gamma_1 = \exp\left[x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2 G_{21}}\right)^2 + \frac{G_{12}\tau_{12}}{(x_2 + x_1 G_{12})^2}\right]\right] \tag{2-1}$$

and

$$\gamma_2 = \exp\left[x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1 G_{12}}\right)^2 + \frac{G_{21}\tau_{21}}{(x_1 + x_2 G_{21})^2}\right]\right]$$

where

$$G_{12} = \exp(-a \cdot \tau_{12})$$

$$G_{21} = \exp(-a \ \tau_{21})$$

$$\tau_{12} = \frac{A12}{T \cdot R}$$

$$\tau_{21} = \frac{A21}{T \cdot R}$$

where

    A12   =   energy parameter describing the chemical interaction between molecules 1 and 2 with respect to 1

    A_{21} =   energy parameter describing the chemical interaction between molecules 2 and 1 with respect to 2

    x_1 =   mole fraction of component 1

    x_2 =   mole fraction of component 2

    α =   nonrandomness factor describing the physical interaction between molecules i and j and how they fit together

    T   =   temperature (°K)

    R   =   gas constant (cal/mol*K).

There are two primary fitting parameters used in the NRTL method. The first is A_{12} (A_{21}), an energy parameter characteristic of the 1-2 (2-1) interaction that accounts for the chemical interaction between molecules 1 and 2. The next parameter, a, is related to the nonrandomness in the mixture. In other words, it accounts for how molecules 1 and 2 fit together physically in the mixture. If the mixture is

completely random (a rare occurrence), a is zero (Henley and Seader 1981). Hence, the parameters A_{12}, A_{21}, and a account for the total molecular interaction between molecules 1 and 2. It is crucial to understand that the physical interaction of molecules is a function of the mole fractions. How molecules fit near either end of dilution is different compared to relatively equal fractions.

Two additional secondary parameters, $\tau_{12}(\tau_{21})$ and $G_{12}(G_{21})$, are calculated based upon the values of A_{12} and a. The τ_{12} factor is an energy parameter that accounts for interaction because of temperature. It is important to note that, since temperature is a function of energy, it is accounted for in the calculation of τ_{12}. The G_{12} energy parameter also incorporates the nonrandomness factor.

Other methods for calculating activity coefficients include the Margules, Van Laar, Wilson, and universal functional activity coefficient (**UNIFAC**) equations.

2.3   Diffusion

For environmental applications, binary liquid diffusion coefficients are primarily used to model contaminant transport through water. Values of diffusion coefficients in water may be estimated using the Wilke-Chang method shown in Equation 2-2 (LaGrega et al. 1994):

$$D = \frac{5.06 \times 10^{-7} \cdot T}{\mu \cdot V^{0.6}} \tag{2-2}$$

where

D =   mutual diffusion coefficient of solute **A** at very low concentrations in water (cm^2/second)

T =   temperature (°K)

μ =   viscosity of water (cP)

V =   molal volume of contaminant (cm^3/molal).

A modified version of the Wilke-Chang equation (shown in Equation 2-3) takes into account an association factor as well as some additional properties of the solvent (Reid, Prausnitz, and Poling 1987):

$$D^{\circ}_{AB} = \frac{7.4 \times 10^{-8} \cdot (\phi \cdot M_B)^{\frac{1}{2}} \cdot T}{\eta_B \cdot V_A^{0.6}} \tag{2-3}$$

where

D^o_{AB} = mutual diffusion coefficient of solute **A** at very low concentrations in solvent B (cm^2/second)

M_B = molecular weight of solvent B (g/mol)

T = temperature (°K)

η_B = viscosity of solvent B (cP)

V_A = mole volume of solute **A** at its normal boiling temperature (cm^3/mol)

ϕ = association factor of solvent B (dimensionless).

There are several other methods that can be used to calculate dilute binary liquid diffusion, but because of its accuracy and ease of use, the modified Wilke-Chang method is most often used, particularly when the solute is less than 5 mole percent (Reid, Prausnitz, and Poling 1987).

Several equations are available for predicting concentration-dependent diffusion coefficients. One of the most often used methods is the modified Darken equation (shown in Equation 2-4) that uses a thermodynamic correction factor, a (Reid, Prausnitz, and Poling 1987):

$$D_{AB} = \left(D^*_A x_A + D^*_B x_B\right) \cdot a \tag{2-4}$$

where

D_{AB} = mutual diffusion coefficient of solute **A** in solvent B (cm^2/second)

D^*_A = tracer diffusion coefficient at x_A and x_B

D^*_B = tracer diffusion coefficient at x_A and x_B

a = thermodynamic correction factor evaluated at x_A and x_B.

Tracer coefficients, which relate to the diffusion of a labeled compound within a homogeneous mixture, are not available in most instances. However, a modification of Equation 2-4 in terms of infinite dilution coefficients is commonly used. Through use of the Wilke-Chang method of estimating dilute diffusion coefficients, concentration-dependent diffusion coefficients can be calculated for use in the modified Darken approach shown in Equation 2-5 (Reid, Prausnitz, and Poling 1987):

$$D_{AB} = \left(D^o_{BA} x_A + D^o_{AB} x_B\right) \cdot \alpha \tag{2-5}$$

where

D_{AB} = mutual diffusion coefficient of solute **A** in solvent B (cm^2/second)

D^o_{AB} = infinitely dilute diffusion coefficient of solute **A** in solvent B (cm^2/second)

D^o_{BA} = infinitely dilute diffusion coefficient of solute B in solvent **A** (cm^2/second).

Another method that is commonly used for ideal or nearly ideal mixtures is the Vignes correlation shown in Equation 2-6:

$$D_{AB} = \left(\left(D_{AB}^{o} \right)^{x_B} \cdot \left(D_{BA}^{o} \right)^{x_A} \right) \cdot a \qquad (2-6)$$

where

D_{AB} = mutual diffusion coefficient of solute A in solvent B (cm^2/second)

D_{AB}^{o} = infinitely dilute diffusion coefficient of solute A in solvent B (cm^2/second)

D_{BA}^{o} = infinitely dilute diffusion coefficient of solute B in solvent A (cm^2/second)

x_B = mole fraction of solvent B

x_A = mole fraction of solvent A

a = thermodynamic correction factor evaluated at x_A and x_B

The behavior of alkanes diffusing through chlorinated solvents, such as carbon tetrachloride, has been well documented. Experimental data have shown that binary diffusion coefficients are strong functions of concentration. It has also been demonstrated that as alkanes increase in chain length, diffusivity decreases and that as branching increases, diffusivity increases (Rowley et al. 1987). However, infinite dilution diffusion coefficients have been shown to be independent of branching but are known to decrease with increasing molecular weight (Rowley et al. 1988).

In many engineering applications, diffusion coefficients are simplified into a generalized form called "effective diffusivity" to avoid the mathematical complexities associated with finding concentration-dependent diffusion coefficients. The effective diffusivity is determined by assuming that the rate of diffusion is dependent on only the concentration gradient of the system (Taylor and Krishna 1993). Effective diffusion coefficients can also be used in systems, whether they are binary or ternary, where the species making up the mixture are of a similar nature (Taylor and Krishna 1993).

2.4 Analytical Method

There are several ways to obtain effective diffusion coefficients. One such method uses a differential equation (shown in Equation 2-7) defining transient heat conduction (Carslaw and Jaeger 1959):

$$\frac{\partial v}{\partial t} = \kappa \cdot \frac{\partial^2 v}{\partial z^2} \qquad (2-7)$$

where

v = temperature

t = time

κ = thermal conductivity

z = position z in interval $0 \leq z \leq L$.

The differential equation is solved for the average temperature in a slab of thickness (L) at time (t) resulting in Equation 2-8 (Carslaw and Jaeger 1959):

$$v_{avg} = \frac{8 \cdot V_o}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n+1)^2} \cdot e^{\frac{-\kappa \cdot (2n+1)^2 \cdot \pi^2 \cdot t}{4 \cdot L^2}} \tag{2-8}$$

where

v_{avg} = average temperature at time (t)

V_o = constant initial temperature

L = slab thickness

By using the heat and mass transfer analogy, diffusivity can be substituted for conductivity and concentration for temperature in situations of similar geometry (shown in Equation 2-9) (Incropera and Dewitt 1996):

$$\frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial z^2} \tag{2-9}$$

where

C = concentration

t = time

D = diffusion coefficient

z = position z in interval $0 \leq z \leq L$.

Equation 2-8 is defined by the boundary conditions of -L < **x** < L for a slab with a temperature of zero at the two surfaces and a constant temperature at the center. In other words, cooling (evaporation) is occurring on both sides of the slab.

Since the equation considers the temperature to be constant at **x** = 0 (the center), the equation can be applied to a dish of 0 < **x** < L as long as the surface at **x** = 0 is a constant temperature (insulated). The application of the heat and mass transfer analogy can be applied to a liquid layer with the boundary conditions of 0 < **x** < L and a constant concentration at the insulated liquid surface (**x** = 0). Substitution of the appropriate constants results in Equation 2-10 (Carslaw and Jaeger 1959):

$$C_{avg} = \frac{8 \cdot C_o}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n+1)^2} \cdot e^{\frac{-D \cdot (2n+1)^2 \cdot \pi^2 \cdot t}{4 \cdot L^2}} \tag{2-10}$$

where

    C_{avg} =   average concentration of solute

    C_o =   initial concentration of solute

    L   =   height of the liquid layer.

This method of quantifying effective diffusion coefficients or bulk mass diffusion coefficients has been demonstrated to be effective for estimating mass loss in a petri dish (Miller 1999). The derivation and discussion of the analytical solution and its associated boundary conditions are found in Appendix B.

The analytical method of estimating effective diffusion coefficients for binary systems will be compared to empirical solutions of the Darken and Vignes equations in the environment of mixed solvents diffusing through TRO. Before using the Darken and Vignes equations, thermodynamic analysis of the various binary pairs will be completed in order to assess the independence of the components in the mix. If any of the chlorinated solvent and TRO binary pairs are proven to be ideal solutions, the thermodynamic correction factor *(a)* used in both equations will simplify to one and can be excluded in the calculations.

3.   MATERIALS AND METHODS

3.1   Approach

As has been discussed in Section 1, significant amounts of chlorinated solvents were buried in approximately 9,680 55-gal steel drums at the SDA. Corrosion of the drums has provided a pathway of release to the environment for the four solvents. One of the first steps in developing a strategy to mitigate release of the chlorinated solvents is to understand the rates of release of the solvents from the waste form. The approach of this study to investigate the rates of release is broken down into four objectives.

The first objective was to determine the independence of diffusion from molecular interactions for the four chlorinated solvents and the TRO in the Series 743 sludge. An approach to deriving independence from molecular interactions is to consider the liquid fraction of the sludge as a combination of all binary pairs. Thermodynamic analysis of the binary pairs will be used to evaluate relative independence of the liquids, expressed in the form of activity coefficients. Since no experimental thermodynamic data were available for TRO, two methods were used to estimate the activity coefficients for the solvent and TRO binary pairs: (1) The UNIFAC method of estimating activity coefficients and (2) the literature data method, using a similar compound. Solvent/solvent binary activities were investigated in keeping with the concept that the mixture is a combination of binary pairs. The intention of the analysis was to investigate whether each binary pair was either ideal or quasi-ideal (activity coefficients equal to one). If the mixture is indeed ideal, the diffusion coefficients can be modeled independently of each other.

The second objective was to calculate diffusion coefficients using both the modified Darken and Vignes equations (empirical approach). Each equation has a thermodynamic correction factor based upon the activity of the binary pairs. Two approaches were taken with each equation. The first was to use actual activity data (objective one) for a compound similar to TRO with each solvent to calculate diffusion coefficients. The second approach was to assume an ideal mixture (confirmed by examining the appropriate binary pair activity coefficients). Ultimately, these diffusion coefficients will be used to confirm the effective diffusion coefficients generated by the analytical solution of transient diffusion.

The diffusion coefficient for each solvent in TRO (estimated by comparative and analytical methods) was compared to experimental data generated by the gravimetric analysis of chlorinated solvents diffusing through and evaporating from TRO. This was done for two separate geometric configurations: one using a petri dish cover and the other using a small aluminum canister.

The third objective was accomplished by evaluating the rate of mass loss of the chlorinated solvents and TRO mixed with calcium silicate from an aluminum canister.

The fourth objective (an additional experiment) was accomplished with chlorinated solvent and TRO mixed with calcium silicate and placed into a sealed container with a single hole (e.g., 1/4 in., 1/8 in., or 1/16 in.) drilled into it. This was done to compare the rate of mass loss from each sized hole, which represents a corroded hole in a 55-gal barrel in the field.

The analytical solution of transient diffusion is based upon the application of the heat and mass transfer analogy to the analytical solution of transient heat conduction. Diffusion from the liquid form of sludge can be estimated by making the appropriate substitutions-effective diffusion for conductivity and mass (concentration) for temperature.

3.2   Materials

Experimental measurements of mass loss caused by the diffusion and subsequent evaporation of each chlorinated solvent through the TRO were used to generate the necessary data for the analytical solution of transient diffusion. Gravimetric collection was automated through the use of a laptop connected through an RS-232 cable to a Mettler-Toledo (Model AT201) self-calibrating balance with Mettler-Toledo data acquisition software. Gravimetric diffusion experiments were performed in a Pyrex Corning petri dish cover (100 x 20 mm) and also in an aluminum canister (3-1/2 in. tall by 1-1/2 in. in diameter).

Calcium silicate was used as a binding matrix for the solvent and TRO binary mixes in aluminum canisters. The same procedure was also performed with binary composition of chlorinated solvent and TRO, mixed with calcium silicate, and placed into a canister with a single-sized escape hole (e.g., 1/4 in., 1/8 in., or 1/16 in.) drilled into the sealed canister.

The chlorinated solvents and the TRO oil used in laboratory studies are listed in Table 3-1. The physical properties of these compounds are listed in Appendix D.

Table 3-1. List of major components found at the Subsurface Disposal Area site.

Chemical	Form/Purity	Manufacturer
Carbon tetrachloride	Liquid / > 99.5%	Sigma chemical
Trichloroethene	Liquid / > 99.5%	Sigma chemical
1,1,1-trichloroethane	Liquid / > 99.5%	Sigma chemical
Tetrachloroethene	Liquid / > 99.5%	Sigma chemical
Texaco Regal Oil 32 oil	Liauid	Texaco Oil. Inc.

It is important to note, for purposes of this study, the use of the terms "solvent" and "solute." Chlorinated solvents, as the name suggests, are commonly used as solvents (e.g., degreasing agents); however, the focus of this study was the mass transport of chlorinated solvents through the TRO. Therefore, the chlorinated solvents are viewed as solutes diffusing through the solvent, TRO.

3.3   Methods

3.3.1   Activity Coefficients

Cumulative molecular interactions between the solvent and the solute must be investigated in order to determine if these interactions affect the rates of diffusion of the solute (i.e., carbon tetrachloride, TCE, TCA, and PCE) through the solvent (TRO). Cumulative interactions between molecules in a solution are described by the activity of each component in the solution, and deviations from ideal solution behavior are expressed as activity coefficients. In the case of an ideal mixture, the activity coefficient is one, and positive or negative deviations from ideality imply repulsive or attractive interactions within the liquid mixture (see Appendix A). Two approaches were taken to determine the activity of TRO.

One approach is to use UNIFAC to estimate the activity of TRO. However, TRO is a proprietary liquid with few published properties (average molecular weight, viscosity, and pour point). Before using UNIFAC, an estimate of the chemical formula of the TRO was completed. The TRO oil is a severely hydroprocessed oil or, in other words, a saturated alkane. According to data provided by Texaco, TRO oil has an average molecular weight of 360 g/mol. Use of the alkane general formula, C_nH_{2n+2}, computes a

minimum chain length of 25 carbons. However, straight-chain alkanes become solids once they exceed a chain length of 17 carbons (Morrison and Boyd 1987). The listed pour point of TRO is −25°F, a low value for a long-chained hydrocarbon. There are two possible reasons for the low pour point: (1) branched alkanes do not fit as tightly together as straight-chain alkanes that line up easily to form a near crystallinelike structure or (2) the introduction of structurally similar but not identical compounds breaks up the crystallinelike structure of the pure compound.

The TRO is known to be a mixture of alkanes with traces of antioxidant material that inhibit rust and oxidation. The antioxidants, however, were ignored in light of their very low concentration (less than 0.01%). In order to simplify the analysis, TRO was modeled as a straight-chain alkane with an average length of 25 carbons and 52 hydrogen atoms ($C_{25}H_{52}$). This assumption provides an average molecular formula that can be used by UNIFAC to estimate the activity of the TRO with the chlorinated solvents.

The UNIFAC method is semitheoretical, estimating activity coefficients for compounds where no experimental data are available. The concept behind UNIFAC is that liquid mixtures are considered to be solutions of structural units from which the molecules are formed rather than a solution of the molecules themselves. These structural units are called subgroups. When the chemical formulas are entered into a UNIFAC program, each chemical compound is broken down into these subgroups. Activity coefficients are then estimated based upon interactions between subgroups and various subgroup properties (Smith, VanNess, and Abbott 1996). Within the UNIFAC program, a regression analysis of experimental data based upon subgroups is used to extrapolate the activity coefficients for binary pairs where no experimental data are available.

HYSYS is a commercially available integrated simulation environment computer program frequently used in industrial plant design. Contained within **HYSYS,** the UNIFAC method of estimating activity coefficients is available in a program format. The appropriate chemical formulas are entered into the UNIFAC program where they are broken down into subgroups and analyzed using the aforementioned regression analysis. The activity data generated in the UNIFAC program can be expressed in the form of the UNIFAC equations, or **HYSYS** can be programmed to fit the data into other solutions that include the NRTL, Margules, Van Laar, and Wilson equations.

The second approach is to use a similar compound for which experimental data are available. The longest alkane chain for which experimental data are available in a binary with each of four chlorinated solvents is n-hexane, a six carbon straight-chained alkane. There is a substantial difference in size of n-hexane (6 carbons) versus TRO (average of 25 carbons). However, both n-hexane and TRO are alkanes with similar structures in that they are composed entirely of carbon and hydrogen atoms arranged as methyl groups and saturated carbon chains having no other polar functional groups. Although TRO is approximately four times the size of hexane, interactions between the chlorinated solvents and hexane should provide some insight as to interactions between the solvents and the TRO.

Additional insight will be provided by analysis of available experimental data for carbon tetrachloride with a variety of alkanes. Within the DECHEMA database, binary activity data are available for carbon tetrachloride with a variety of straight and branched alkanes (Gmehling, Onken, and Arlt 1980a; Gmehling, Onken, and Arlt 1980b). This analysis will be used to investigate trends in activity coefficients for carbon chains increasing in both length and branching. These trends will assist in extrapolating the range of possible activity coefficients for TRO.

Solvent/solvent interactions also must be considered to complete the analysis of binary mixtures in the liquid fraction of Series 743 sludge. Four of the six possible combinations are available as experimental data in the DECHEMA database. The remaining two combinations were estimated using UNIFAC.

Activity data within the DECHEMA series are commonly listed in the form of NRTL parameters. Therefore, all estimates of activity data from UNIFAC are programmed in **HYSYS** to be produced in the form of NRTL parameters (see Appendix E).

3.3.2 Binary Diffusion Estimation (Empirical Approach)

Multicomponent diffusion, particularly that of interacting compounds, is difficult to model because of the potential complexity of the range of interactions present in the mix (Taylor and Krishna 1993). However, diffusion of the compounds can be modeled as independent functions if the liquid mixture of waste is shown to be ideal or close to ideal.

An approach to describing multicomponent diffusion is to consider the mixture to be a set of binary systems. By evaluating the various components of binary diffusion, the components of ternary diffusion may be better understood. The modified Darken and Vignes equations were used to calculate concentration-dependent diffusion coefficients for each binary pair. Effective diffusion coefficients have been defined as 'average diffusion over a given range of concentration' (Taylor and Krishna 1993). A simplistic approach of estimating effective diffusion coefficients is completed by taking an average diffusion value over the given concentration range of each chlorinated solvent.

The Wilke-Chang equation is a commonly used method for estimating infinite dilution diffusion coefficients (shown in Equation 3-1) (see Section 2, Equation 2-2):

$$D^o_{AB} = \frac{7.4 \times 10^{-8} \cdot (\phi \cdot M_B)^{\frac{1}{2}} \cdot T}{\eta_B \cdot V_A^{0.6}} \tag{3-1}$$

As discussed in Section 2, infinite dilution diffusion coefficients are required in both the modified Darken and Vignes equations. Two parameters found in the equation must be estimated in order to use the equation. The first property to be estimated is V_A, the molar volume of solute A at its normal boiling temperature. There are several methods used to estimate V_A, including the Le Bas and the Schroeder methods (Reid, Prausnitz, and Poling 1987). The Schroeder method was used here because of its higher degree of accuracy (see Appendix F).

Predicted values for the chlorinated solvent molar volumes are reportedly accurate to within 3% (Reid, Prausnitz, and Poling 1987). The Schroeder method is based upon the type of atom contained within the molecule, rather than on structural groups within a molecule, with the exception of ringed compounds. Therefore, a high degree of accuracy is given to the approach because of the simple nature of the compounds in question (saturated hydrocarbons). The TRO molar volume is based upon the estimated chemical formula.

The association factor (ϕ) is based upon the type of solvent used. Values are listed for solvents such as methanol, ethanol, and water. Alkanes as solvents are considered to be unassociated liquids. The value of one is used for the association factor in unassociated solvents and is therefore used for TRO (Bird, Stewart, and Lightfoot 1960). Dilute diffusion coefficients were calculated for each binary in the mixture using the Wilke-Chang method.

Two approaches were taken to estimate the concentration-dependent diffusion coefficient for the modified Darken and the Vignes equations. The first was to use the activity data of the solvent-hexane binary pairs as a proxy for the thermodynamic correction factor for the solvent-TRO binary pairs. The second approach is to assume that the mixture is ideal ($a = 1$).

Before using the hexane activity data to calculate diffusion coefficients, the thermodynamic correction factor, a, had to be calculated for both equations. The thermodynamic correction can be calculated by using the following equation (Valsaraj 1995):

$$\alpha = \left[\frac{\partial \ln a}{\partial \ln x} \right]_{T,P}$$

(3-2)

where

    a   =   activity of A or B component

    x   =   mole fraction of A or B component.

It is important understand from the Gibbs-Duhem equation that Equation 3-2 is the same whether it is written for Liquid A or B (Reid, Prausnitz, and Poling 1987). The Gibbs-Duhem equation states that activity coefficients of individual components of a multicomponent system are not independent of one another but are related by a differential equation. This relation is written for a binary mixture shown in Equation 3-3 (Reid, Prausnitz, and Poling 1987):

$$x_A \cdot \left(\frac{\partial \ln \gamma_A}{\partial x_A} \right)_{T,P} = x_B \cdot \left(\frac{\partial \ln \gamma_B}{\partial x_B} \right)_{T,P} .$$

(3-3)

where

    x_A =   mole fraction of A component

    x_B =   mole fraction of B component

    γ_A =   activity coefficient of A component

    γ_B =   activity coefficient of B component.

The activity coefficient, γ, is related to the activity by Equation 3-4 (Smith, VanNess, and Abbott 1996):

$$a_i = \gamma_i \cdot x_i .$$

(3-4)

This equation is substituted into Equation 3-2 and, when integrated, results into what is commonly known as the thermodynamic factor, Γ, shown in Equation 3-5 (Valsaraj 1995):

$$\Gamma = 1 + x_i \frac{\partial \ln \gamma_i}{\partial x_i}$$

(3-5)

In other words, $\Gamma = a$ when the fugacities approach unity, and the equation for Γ can be substituted for the thermodynamic correction factor, a, in both the modified Darken and Vignes equations (Taylor and Krishna 1993).

The modified Darken equation (shown in Equation 3-6) incorporates infinite dilution diffusion coefficients, mole fractions, and the thermodynamic correction factor to calculate concentration-dependent diffusion coefficients (Section 2, Equation 2-5):

$$D_i = \left(D_{BA}^{\circ} x_A + D_{AB}^{\circ} x_B \right) \cdot \alpha \quad . \tag{3-6}$$

Infinite dilution diffusion coefficients were calculated using the Wilke-Chang equation. The thermodynamic correction factor (*a*)at ambient conditions has been simplified to the thermodynamic factor (Γ). All components of the modified Darken equation are known, and diffusion coefficients can be calculated as functions of mole fractions. It is important to note that the thermodynamic factor is also a function of the mole fraction.

The Vignes equation incorporates the same variables as the modified Darken equation. The difference between the equations (shown in Equation 3-7) is the use of the mole fractions as power functions (Section 2, Equation 2-6):

$$D_i = \left(\left(D_{AB}^{\circ} \right)^{x_B} \cdot \left(D_{BA}^{\circ} \right)^{x_A} \right) \cdot a \tag{3-7}$$

Diffusion coefficients for all four solvent-TRO binary pairs were calculated using both the Darken and Vignes equations. Effective diffusion coefficients were calculated by taking an average diffusion coefficient over the mole fraction range of the chlorinated solvents.

The starting mole fraction of each solvent in TRO is calculated by considering the starting volumetric 2-1 ratio of solvent to TRO at time zero. The mass of each component was calculated by multiplying the given volume by the appropriate density. The starting mole fraction was calculated for each solvent by dividing the mass of each component by its molecular weight. The starting mole fraction for each solvent calculates to be a uniform value of 0.9. In other words, 90% of the moles in solution are chlorinated solvent. At the time of complete evaporation, all of the chlorinated solvent has evaporated leaving behind pure TRO. At this point, the mole fraction of TRO is one, and the mole fraction of the chlorinated solvent is zero. The range of mole fractions for the chlorinated solvents is 0.9 (at time zero) to 0.0 (at the time of complete evaporation).

3.3.3   Experimental Design and the Analytical Method

Gravimetric analysis experiments were completed for each solvent-TRO binary pair. The TRO in previous research has been shown to be nonvolatile in the range of environmental temperatures (Miller 1999). Therefore, all mass loss is attributed to the transport of the chlorinated solvent through diffusion to the top of the liquid surface where it subsequently evaporates.

The volumetric ratio of solvent to TRO (2:1) was used to represent the ratio of solvent to TRO in the liquid waste of 743 Series sludge. For all four binary mixtures, 66.6 mL of chlorinated solvent were added to 33.3 mL of TRO. Mixing was done in a graduated cylinder to minimize evaporative losses. The graduated cylinder was covered with a rubber glove and inverted four consecutive times to mix the sample. The sample was immediately poured into a preweighed vessel and then into either a petri dish or an aluminum canister and placed on the Mettler-Toledo balance. Incremental mass readings were taken at 15-minute intervals thereafter for a period 5 days by means of the automated data-acquisition software. Afterward, the mass balance readings were recorded once daily or every 2 days until mass readings remained stable throughout the experiment.

This procedure was repeated for each solvent in a sludge matrix formed by mixing 20 g of calcium silicate with the solvent-TRO binary. The mass loss readings were recorded in a spreadsheet for analysis. These procedures were performed in duplication for each chlorinated solvent-TRO binary mixture with and without calcium silicate to assess repeatability of the results.

A similar procedure was performed for the binary chlorinated solvent-TRO pair with calcium silicate contained in a sealed aluminum canister with a single hole (e.g., 1/4 in., 1/8 in., or 1/16 in.) in the capped canister. Mass loss readings were again recorded in a spreadsheet for analysis. These experiments were also performed in duplication to assess the repeatability of the results.

To determine diffusion coefficients in a multicomponent (ternary) system, a mixture of the four solvents with TRO was made by mixing equal volumes of solvent with TRO in the same 2-1 ratio of solvent to TRO used in the binary experiments (66 to 33 mL). Because of the presence of four evaporating solvents in the petri dish, gravimetric analysis cannot account for the loss of each individual component in the ternary mixture. Therefore, GC/MS analysis was used to find the concentrations for each component in order to determine mass loss. This was performed with only one physical configuration (petri dish) and did not include any of the calcium silicate matrix.

Diffusion experiments were left undisturbed to prevent convection and other forms of induced mixing that would affect the rates of diffusion. Therefore, multiple dishes were set up that were sacrificed at specified times for gas chromatography analysis. For this study, 15 dishes were set up, and one was sacrificed approximately every **8** hours covering a period of 5 days. In this manner, relative remaining mass fractions could be calculated from the concentration data generated by the GC/MS analysis.

The method of sampling the ternary mixture consisted of pouring the contents of the sacrificial petri dish into a 50-mL beaker and mixing the solution for a period of 15 seconds. Using a clean pipette, a 2-mL vial with a teflon septum was filled to the brim to eliminate dead air space. This was necessary to prevent solvent evaporation that would alter the composition of the liquid. All collected samples were stored in a refrigerator at 2°C before analysis. When all samples were collected, they were packed with ice into a cooler and sent to the INEEL for GC/MS analysis.

The analytical solution of transient diffusion (shown in Equation 3-8) (Carslaw and Jaeger 1959) contains only three independent variables that are accounted for before its application (Section 2, Equation 2-10):

$$C = \frac{8 \cdot C_o}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{\frac{-D \cdot (2 \cdot n+1)^2 \cdot \pi^2 \cdot t}{4 \cdot L^2}} \tag{3-8}$$

The first variable is L, which in this situation, is taken to be two-thirds of the liquid height. The value of two-thirds represents the average value of the height of the liquid between time zero and the time of complete evaporation (see Appendix B). The second variable is the time, which must be entered as seconds to maintain consistency of units (units of the effective diffusion coefficient are cm^2/second). The third variable is the initial concentration. To simplify the fitting of the analytical solution of transient diffusion to the experimental data, each side of the equation is divided by the starting concentration (C_o). The result is a new equation (shown in Equation 3-9) that solves for the relative remaining mass fraction, ω:

$$\omega = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{\frac{-D \cdot (2 \cdot n+1)^2 \cdot \pi^2 \cdot t}{4 \cdot L^2}} \tag{3-9}$$

Whether units of concentration or mass are used, division of the initial quantity by the remaining quantities results in relative remaining mass fractions at any given time interval. The relative remaining mass fraction was set at an initial value of one, since the initial concentration (mass) is the same as the average starting concentration (mass) at time zero. Using a spreadsheet, the analytical solution was fit to the gravimetric data from the binary petri dish experiments by adjusting the effective diffusion coefficient to minimize the mean squared difference between the predicted and measured values of relative remaining mass fractions.

It is important to note that all mass loss in the dish is attributed to solvent evaporation. Therefore, the remaining mass fraction of solvent was calculated by simply dividing the solvent mass at time (t) by the initial mass reading at time zero. For the ternary mixtures, the mass loss was recorded as concentration changes. Relative remaining mass fractions were calculated by dividing the concentrations at time (t) by the concentration at time zero. The analytical solution of transient diffusion was fitted to the data at the recorded time intervals. In a similar fashion, the analytical solution was fit to the data for the ternary mix by adjusting the effective diffusion coefficient.

4.   RESULTS AND DISCUSSION

4.1   Overview

The first objective of this study was to investigate the degree of cumulative interactions of the liquid fraction of Series 743 sludge by considering the activity coefficients of each possible binary pair. The UNIFAC equation was used to estimate the activity of the chlorinated solvent-TRO binary pairs. Literature values of activity coefficients for solvent-hexane binary pairs were used as another method of estimating chlorinated solvent-TRO activity coefficients. Analysis of carbon tetrachloride, alkane activity with a variety of long-chain and branched alkanes was completed to provide additional insight into the interaction of the chlorinated solvents with TRO. Four of the six solvent/solvent binary pair activity data were available in the literature; the remaining two were predicted by UNIFAC. All activity data were expressed in the form of NRTL parameters.

For the second objective, effective diffusion coefficients were estimated mathematically by taking an average value of the diffusion coefficient over the given mole fraction range for each chlorinated solvent-TRO binary pair using the modified Darken and Vignes equations. Two approaches were taken with each equation. The first approach used the activity of the solvent-hexane binary pairs as a proxy for the activity of the solvent-TRO binary pairs. In the second approach, the mixture was considered to be an ideal mixture (justified by activity coefficients of unity). Diffusion coefficients were graphed as a function of mole fractions.

The analytical solution of transient diffusion from Carslaw and Jaeger (1959) was fitted to gravimetrically determined mass-remaining values for the four chlorinated solvent-TRO binary pairs in two separate physical configurations (petri dish and aluminum canister). Concentration data from a ternary mixture composed of all four solvents and TRO evaporated from a petri dish were also fitted to the analytical solution of transient diffusion. An effective diffusion coefficient for each binary of chlorinated solvent and TRO was fitted by adjusting its value to minimize the mean squared difference between the experimental data and the resulting analytical curve.

Results of the empirical approach were used to validate the effective diffusion coefficients obtained by fitting the analytical solution of transient diffusion to the experimental data. It is difficult to estimate effective diffusion coefficients to within an order of magnitude (Taylor and Krishna 1993). Given this difficulty, if the analytical solution of transient diffusion and the empirical methods generate values of the effective diffusion coefficient that are within an order of magnitude, the analytical values are deemed to be reliable estimates of diffusion.

The third objective, that of evaluating the effect of the calcium silicate matrix, was determined by gravimetric analysis of chlorinated solvent-TRO binary compositions mixed with matrix in an aluminum canister. The results were compared to identical binary compositions without calcium silicate in aluminum canisters. An approximation of an effective diffusion coefficient for each solvent-TRO pair mixed with calcium silicate was determined by applying the analytical solution for transient diffusion to the results. However, including the effect of the calcium silicate matrix in the determination of an effective diffusion coefficient is used here only for comparative purposes. The analytical solution was developed for a liquid-liquid model and does not account for the possible interactions of the calcium silicate matrix with the solvent-TRO pairs. The effective diffusion coefficients found for the mixtures with calcium silicate are used to provide numerical values of comparison only with the results obtained from solvent-TRO binary pairs.

For the find objective, gravimetric analysis of mass loss from canisters with a single-sized escape hole will be wed to evaluate the effect of hole size on the rate of solvent mass loss. From this, one might scale up and estimate the length of time for solvent to escape from a 55-gal drum.

4.2 Results of the Activity Analysis

Figures 4-1 through 4-8 graphically display both the UNIFAC estimations and literature collections of the activities of the various solvent-TRO and solvent-hexane binary pairs. Figure 4-1 predicts small negative deviations from ideality for the carbon tetrachloride, TRO binary as carbon tetrachloride approaches an activity coefficient value of 0.5, and TRO approaches an activity value of 0.25 near infinite dilution. Figure 4-2, however, demonstrates small positive deviations for the carbon tetrachloride, hexane binary. Of particular interest is the limited expression of activity for carbon tetrachloride. As previously mentioned in Section 3, the starting mole fraction of carbon tetrachloride is 0.9. As can be seen in Figure 4-2 (carbon tetrachloride and hexane), at this mole fraction, the activity coefficient of carbon tetrachloride is very near one (qui—ideal) and as it approaches infinite dilution, reaches a maximum deviation of the activity coefficient of only 1.25. As the mole fraction of carbon tetrachloride approaches infinite dilution $(x_1 = 0)$, the resulting activity coefficient does not exceed 1.25. At such low mole M o n s, the physical expression of activity (increase in escaping potential, see Appendix A) is minimized.
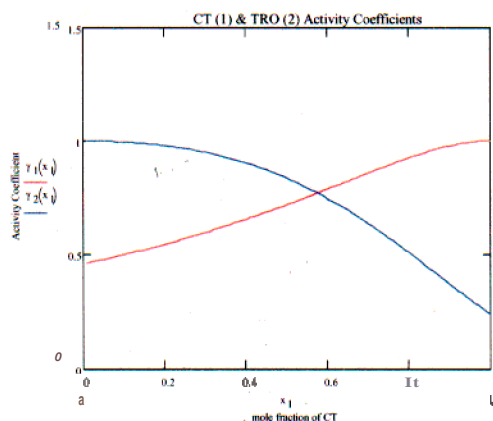

Figure 4-1. Universal functional activity coefficient estimations of carbon tetrachloride, Texaco Regal Oil activity coefficients.
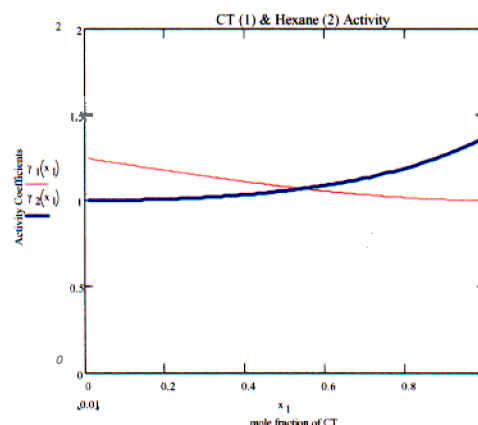
Figure 4-2. DECHEMA carbon tetrachloride, hexane activity coefficients.

The difference between Figures 4-3 (TCE and TRO) and 4-4 (TCE and hexane) is similar to those differences found with Figures 4-1 (carbon tetrachloride and TRO) and 4-2 (carbon tetrachloride and hexane). Figure 4-3 (TCE and TRO) shows small negative deviations from the ideal situation, and Figure 4-4 (TCE and hexane) demonstrates small Uniform positive deviations toward infinite dilutions for both components. Although the activities are different between hexane and TRO, both the literature data and the UNIFAC estimation demonstrate that both carbon tetrachloride and TCE interact with each alkaline (TRO and hexane) in a similar fashion. Although the activity for TCE and hexane is slightly larger than that of carbon tetrachloride and hexane, they are still relatively small when considering they both deviate very little from one until they approach infinite dilution where the expression of activity is limited by the low values of mole fraction.

Figure 4-3. Universal functional activity coefficient estimations of trichloroethene, Texaco Regal Oil activity coefficients.

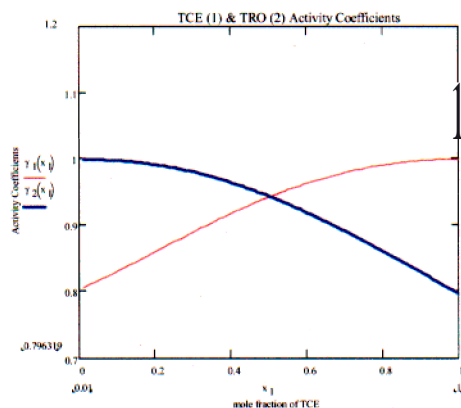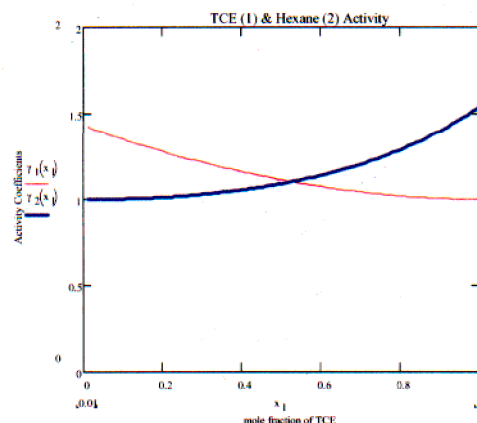**Figure 4-4.** DECHEMA trichloroethene, hexane activity coefficients.

Contrary to the trends seen in Figures 4-1 (carbon tetrachloride and TRO) and 4-3 (TCE and TRO), the UNIFAC method in Figure 4-5 (TCA and TRO) predicts small positive deviations from ideality with an increase in the activity of TCA at high mole fractions of TRO.

Figure 4-6 (TCA and hexane) is almost a copy of Figure 4-4 (TCE and hexane), which suggests that TCE and TCA interact with hexane in a similar manner. Although Figure 4-2 (carbon tetrachloride and hexane) is not identical, it is similar to Figures 4-4 (TCE and heme) and 4-6 (TCA and hexane) with the presence of small positive deviations in the activity of both compounds as they approach infinite dilution.

Figure 4-5. Universal functional activity coefficient estimations for 1,1,1-trichloroethane, Texaco Regal Oil activity coefficients.

Figure 4-6. DECHEMA 1,1,1-trichloroethane, hexane activity coefficients.

In Figure 4-7 (PCE and TRO), UNIFAC predicts small negative symmetrical deviations toward infinite dilution, whereas in Figure 4-8 (PCE and hexane), the literature data indicate the opposite in predicting positive symmetrical deviations toward infinite dilution. In Figures 4-1 (carbon tetrachloride and TRO), 4-3 (TCE and TRO), 4-5 (TCA and TRO), and 4-7 (PCE and TRO), UNIFAC predicts negative deviations for three of the four chlorinated solvents with little indication that the interactions are in any way similar. A comparison of Figures 4-2 (carbon tetrachloride and hexane), 4-4 (TCE and

hexane), 4-6 (TCA and h e m e), and 4-8 (PCE and hexane) reveals that the four chlorinated solvents interact with hexane in a similar manner. This trend of similarity among the activity coefficients of the chlorinated solvent-hexane binary pairs should theoretically repeat itself with the solvent-TRO binary pair based upon the similarity of structure between hexane and TRO (saturated hydrocarbons).
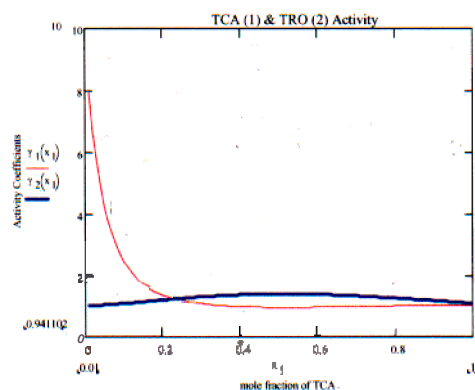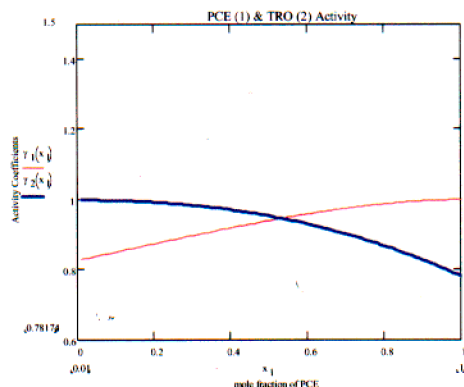

Figure 4-7. Universal functional activity coefficient estimations of tetrachloroethene, Texaco Regal Oil activity coefficients.
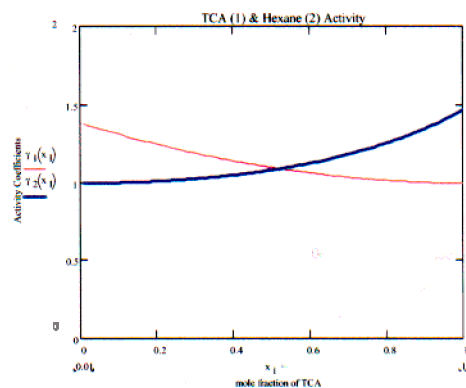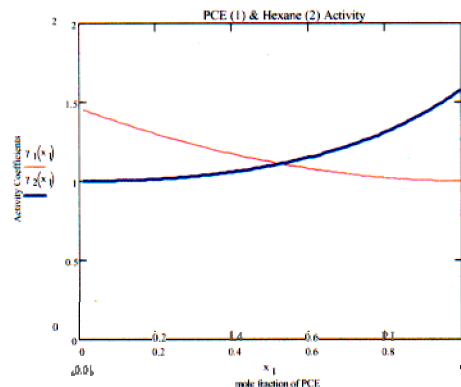
Figure 4-8. DECHEMA tetrachloroethene, hexane activity coefficients.

Additional activity data for carbon tetrachloride with a variety of different alkanes are available in the DECHEMA database. A variety of alkanes, both straight chained and branched, was analyzed to determine what trends exist with the chlorinated solvents as both the chain length and the degree of branching increased.

Figure 4-9 (carbon tetrachloride and heptane) reveals a further decrease in the activity coefficients when carbon tetrachloride is mixed with an alkane with one more carbon than hexane (*compare* to Figure 4-2 [carbon tetrachloride and hexane]). This trend continues with the mixture of carbon tetrachloride and octane, which results in an almost ideal mixture demonstrated by a straight line seen in Figure 4-10.
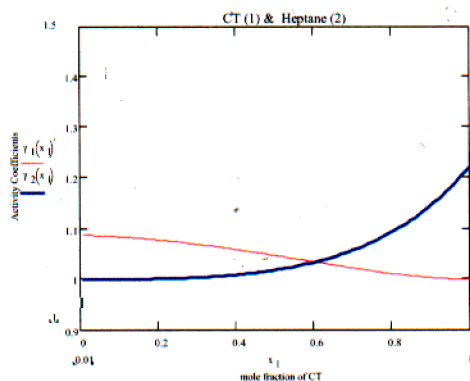
Figure 4-9. DECHEMA carbon tetrachloride, heptane activity coefficients.
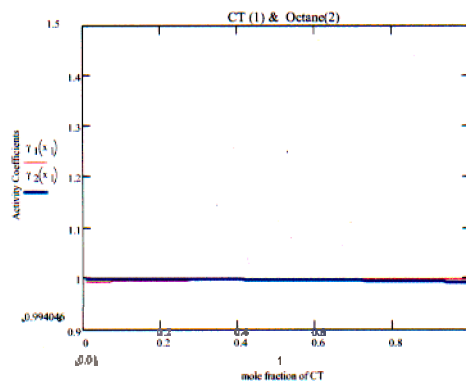
Figure 4-10. DECHEMA carbon tetrachloride, octane activity coefficients.

Figure 4-11 reveals a curve very similar to that of the carbon tetrachloride, heptane binary when carbon tetrachloride is mixed with nonane. This binary may reveal a breaking of the trend of decreasing activity with increasing chain length. However, this trend may hold true in that odd-numbered alkanes

may interact slightly differently than even-numbered alkanes, yet the overall trend is still an approach toward ideality with increasing chain length, different degrees, and *odd-* and even-numbered alkanes.
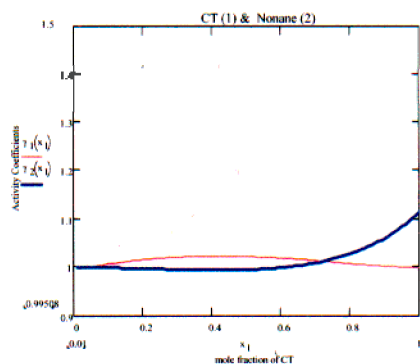
Figure 4-11. DECHEMA activity coefficients for carbon tetrachloride and nonane.
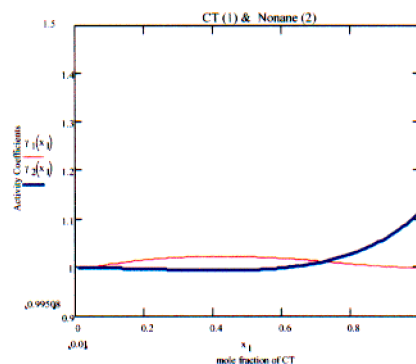
Figure 4-12. DECHEMA activity coefficients for carbon tetrachloride and hexadecane.

The binary mixture of carbon tetrachloride and hexadecane demonstrates small negative deviations from ideality. The presence of this negative deviation with a long-chain alkane provides m e support to the UNIFAC predictions of negative deviations with the solvent-TRO binary pairs in Figures 4-1 (carbon tetrachloride and TRO), 4-3 (TCE and TRO), and 4-7 (PCE and TRO).

Close observation of Figures 4-13, 4-14, and 4-15 demonstrates a trend of decreasing activity in branched alkane chains of increasing length. A near-ideal mixture occurs in the case of the carbon tetrachloride and 2,2,5-trimethylhexane binary, It is important to note that 2,4–dimethylpentane and 2,2,4–trimethylpentane are isomers of heptane and octane, respectively. The branched alkanes demonstrate a slight increase in activity compared to their straight-chained counterparts in the area where the carbon tetrachloride mole fraction approaches purity (mole fraction = 1) but still remains insignificant enough to consider the mixtures ideal.
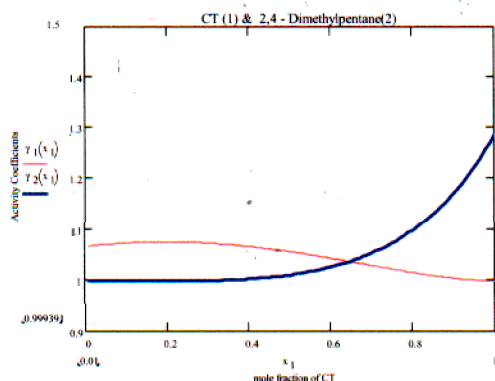
Figure 4-13. DECHEMA carbon tetrachloride, 2,4-dimethylpentane activity coefficients.
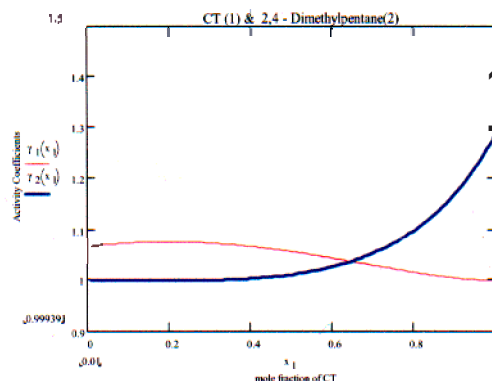
Figure 4-14. DECHEMA carbon tetrachloride, 2,2,4-trimethylpentane activity coefficients,
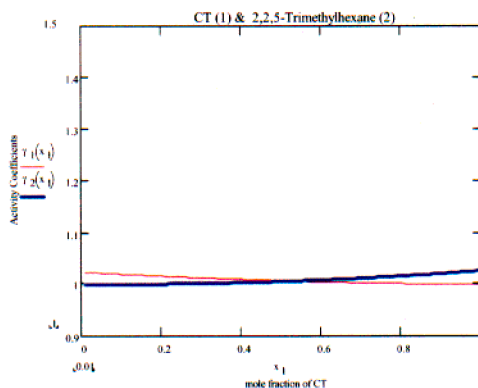
Figure 4-15. DECHEMA carbon tetrachloride, 2,2,5-trimethylhexane activity coefficients,

The liquid fraction of waste material in the SDA site is *composed* of TRO and the four chlorinated solvents. In addition to the four solvent-TRO binary pairs, there are *six* additional solvent/solvent binary pin that must be accounted for: carbon tetrachloride and TCE, carbon tetrachloride and TCA, carbon tetrachloride and PCE, TCE and PCE, TCE and TCA, and TCA and PCE. Literature data are available for four of the listed binary pairs. The UNIFAC equation is used to estimate the activity of the TCE-TCA and TCA-PCE binary pairs.

As can be seen in Figure 4-16, the resulting carbon tetrachloride, TCE activity coefficients curves do not deviate much from one. In Figure 4-17, the resulting activity curves for the carbon tetrachloride, TCA binary show some small increases in the activity coefficient of TCA as it approaches infinite dilution.
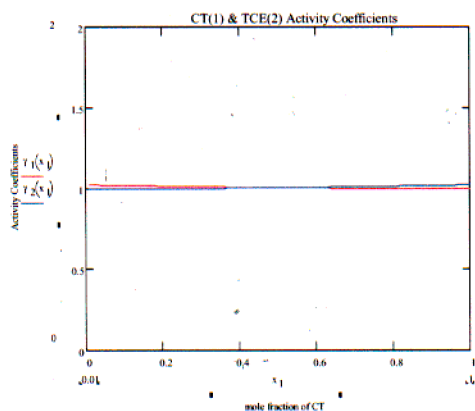
Figure 4-16. DECHEMA carbon tetrachloride, trichloroethene activity coefficients.
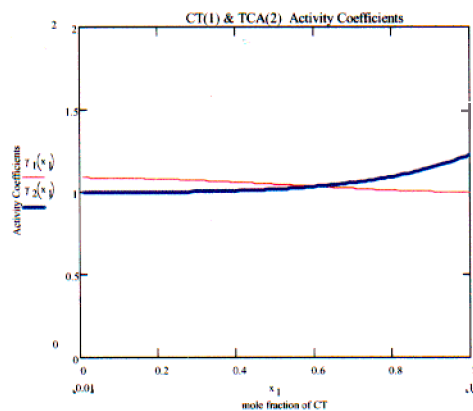
Figure 4-17. DECHEMA carbon tetrachloride, 1,1,1-trichloroethane activity coefficients.

The activity coefficients in Figure 4-18 (carbon tetrachloride and PCE) are virtually identical to the activity coefficients in Figure 4-16 (carbon tetrachloride and PCE) where each is a virtual straight line. Figure 4-19 (TCE and PCE) demonstrates some positive deviations in activity compared to the other three solvent/solvent binary pair, yet in relative terms, it is still virtually ideal.
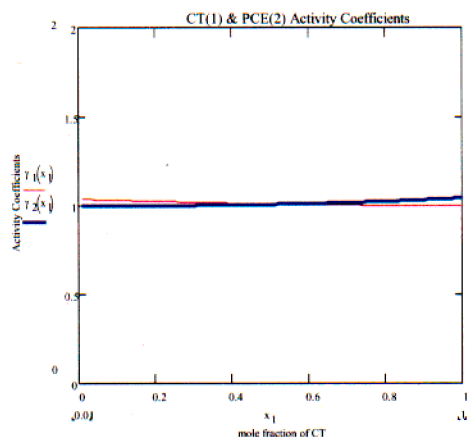
Figure 4-18. DECHEMA carbon tetrachloride, tetrachloroethene activity coefficients.
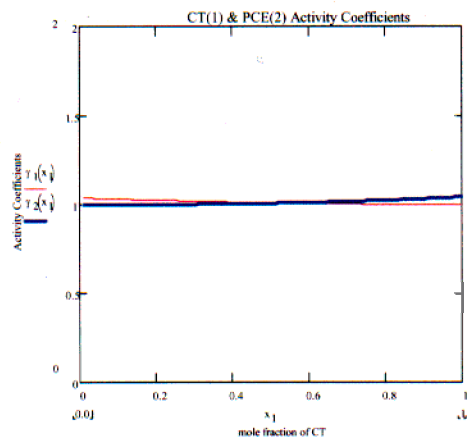
Figure 4-19. DECHEMA trichloroethene, tetrachloroethene activity coefficients.

The UNIFAC was used to estimate the activity of the TCE-TCA and TCA-PCE binary pairs. As can be seen in Figure 4-20 (TCE and TCA), UNIFAC predicts small negative deviations from ideality, whereas in Figure 4-21 (TCA and PCE), UNIFAC predicts the largest positive deviations seen in the activity coefficients of the six solvent/solvent binary pairs. Still, the deviations in Figure 4-21 (TCA and PCE) are considered to be near ideal.
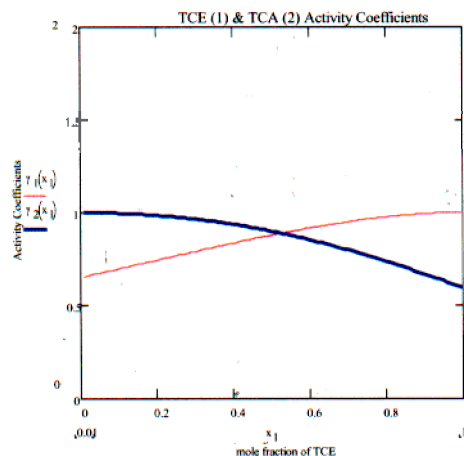
Figure 4-20. Universal functional activity coefficient estimations of trichloroethene, tetrachloroethene activity coefficients.
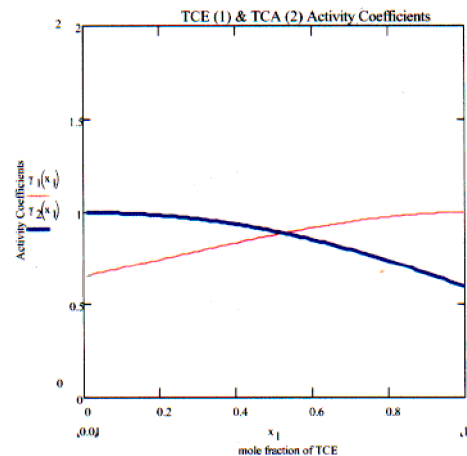
Figure 4-21. Universal functional activity coefficient estimations of 1,1,1-trichloroethane, tetrachloroethene activity coefficients.

4.3   Discussion of the Activity Analysis

From analysis of the activity coefficient estimates, there is strong evidence to support the hypothesis that the liquid fraction of Series 743 sludge is either a quasi-ideal or an ideal mixture. Analysis of the chlorinated solvent-heme data demonstrates limited positive deviations from ideality for each

binary pair. The use of the estimated chemical formula of TRO in UNIFAC implied that long-chain alkanes may result in negative deviations from ideality when mixed with these solvents. This trend is seen in the analysis of the activity coefficients of carbon tetrachloride and hexadecane, which show small negative deviations.

It has been determined that the TRO is actually a mixture of alkanes of varying lengths and shapes. Analysis of carbon tetrachloride with alkanes of varying shapes revealed two trends: (1) a general decrease of activity as chain length increases and (2) a general decrease of activity as branching increases. These trends imply that the chlorinated solvent-TRO binary pairs are close to being ideal solutions. This conclusion is supported by earlier work that suggests that combinations such as these are either slightly positive (quasi-ideal) or ideal (Henley and Seader 1981).

Experimental solvent/solvent activity data also did not demonstrate any significant deviations from ideality. The UNIFAC equation reveals some small negative deviations for the TCE-PCE binary pair and positive deviations for the TCA-PCE binary. In some cases, no deviations from ideality were seen.

The lack of any significant activity in any one of the possible binary combinations provides strong evidence to the hypothesis that the liquid fraction of Series 743 sludge can be considered an ideal solution.

4.4   Results of the Empirical Methods

Infinite dilution coefficients were calculated using the Wilke-Chang estimation method before using the modified Darken and Vignes equations to estimate concentration-dependent diffusion coefficients for the solvent-TRO binary pairs (Reid, Prausnitz, and Poling 1987). The results are listed in Table 4-1.

Table 4-1. Wilke-Chang estimation of infinitely dilute diffusion coefficients at 21°C for solvent Texaco Regal Oil mixtures (cm^2/second).

$D_{CT.TRO} = 3.93E-7$	$D_{TCE.TRO} = 3.941E-7$	$D_{TCA.TRO} = 3.787E-7$	$D_{PCE.TRO} = 3.583E-7$
$D_{TRO.CT} = 6.20E-6$	$D_{TRO.TCE} = 9.755E-6$	$D_{TRO.TCA} = 6.667E-6$	$D_{TRO.PCE} = 6.937E-6$

In the activity coefficient section of this report, the hexane analogy was used to compare the TRO-volatile-organic-compound (VOC) activity data. In following the analogy, infinitely dilute diffusion coefficients were calculated using the Wilke-Chang method with hexane substituted for TRO. Table 4-2 lists the dilute diffusion coefficients for the hexane-VOC mixtures.

Table 4-2. Wilke-Chang estimation of infinitely dilute diffusion coefficients at 21°C for solvent-hexane mixtures (cm^2/second).

$D_{CT.hex} = 3.601E-5$	$D_{TCE\,hex} = 3.612E-5$	$D_{TCA\,hex} = 3.47E-5$	$D_{PCE.hex} = 3.283E-5$
$D_{hex\,CT} = 1.243E-5$	$D_{hex.TCE} = 1.955E-5$	$D_{hex\,TCA} = 1.336E-5$	$D_{hex.PCE} = 1.391E-5$

There is a literature value of the infinitely dilute diffusion coefficient of carbon tetrachloride diffusing through n-hexane of $3.70E-5$ cm^2/second (Reid, Prausnitz, and Poling 1987). The calculated value of $3.601E-5$ cm^2/second is within 3% of the literature value. This small difference between the measured and theoretical values demonstrates the effectiveness of using the Wilke-Chang equation to estimate infinitely dilute diffusion coefficients.

Concentration dependent diffusion coefficients were calculated by using the modified Darken equation shown in Equation 4-1 (Section 2, Equation 2-5):

$$D_{AB} = \left(D^o_{BA} x_A + D^o_{AB} x_B \right) \cdot a \quad . \tag{4-1}$$

The infinitely dilute diffusion coefficients (the Wilke-Chang calculations) were incorporated into the modified Darken equation. Two sets of diffiion coefficients using the modified Darken were calculated. The first set used the thermodynamic data generated from the literature values of solvent-hexane activity. The second set used the assumption of an ideal mixture ($a = 1$). The modified Darken calculations of the diffusion coefficients were graphed as a function of mole fraction. The results are presented in Figures 4-22 through 4-25.

Figure 4-22. Diffusion of carbon tetrachloride, Texaco Regal Oil using hexane, and ideal behavior.

Figure 4-23. Diffusion of trichloroethene and Texaco Regal Oil using hexane and ideal behavior.

Figure 4-24. Diffiion of 1,1,1-trichloroethane and Texaco Regal Oil using hexane and ideal behavior.

Figure 4-25. Diffusion of tetrachloroethene and Texaco Regal Oil using hexane and ideal behavior.

The straight lines ($\alpha = 1$, ideal) shown in Figures 4-22 through 4-25 demonstrate that the diffusion coefficient is a linear function of concentration in an ideal mixture. Small decreases in the values of diffusion are shown when the activity data for the chlorinated-hexane binary pairs are used in the thermodynamic correction factor. The largest decrease in *the* value of the diffiion coefficient is seen in Figure 4-23 (TCE and TRO). In relative terms, comparison of these graphs reveals that use of the activity

data of the chlorinated solvent-hexane binary pairs as a substitute for solvent-TRO activity results in only small decreases in the value of the diffusion coefficient.

The Vignes equation (using mole fractions as power functions) presents an alternative equation (shown in Equation 4-2) for estimating concentration-dependent diffusion coefficients (Section 2, Equation 2-6):

$$D_{AB} = \left(\left(D_{AB}^o \right)^{x_B} \cdot \left(D_{BA}^o \right)^{x_A} \right) \cdot \alpha \quad . \tag{4-2}$$

The activity correction factor was used in an identical fashion to the Darken equation. Infinitely dilute diffiion coefficients calculated by the Wilke-Chang equation are incorporated into the Vignes equation. Concentration dependent diffusion coefficients were calculated and graphed as functions of mole fractions. The results are presented in Figures 4-26 through 4-29.

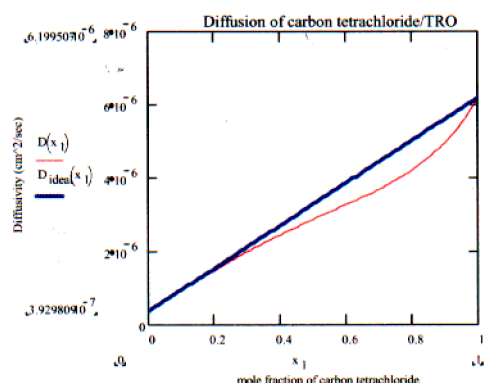Figure 4-26. Diffusion of carbon tetrachloride, Texaco Regal Oil using hexane, and ideal behavior.
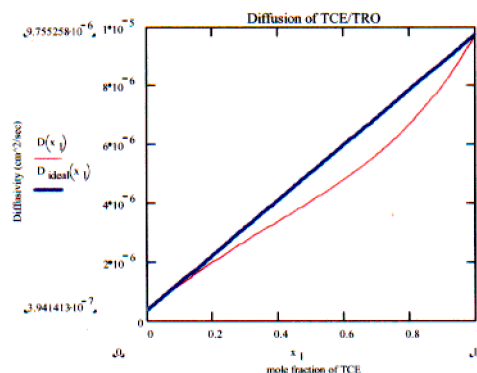

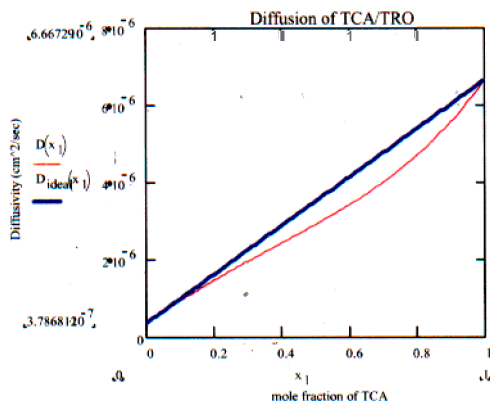Figure 4-27. Diffusion of trichloroethene and Texaco Regal Oil using hexane and ideal behavior.

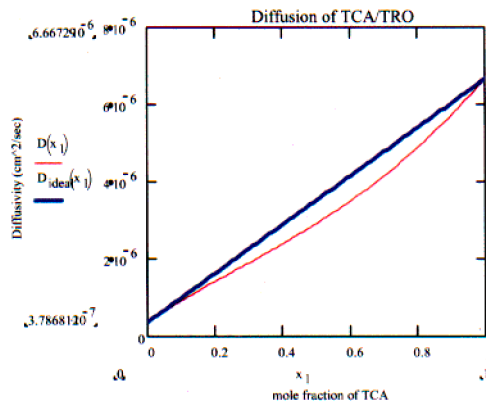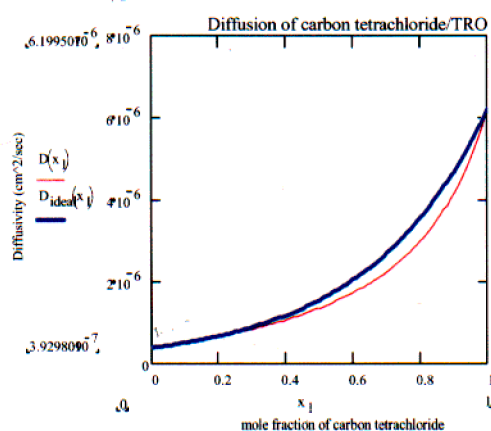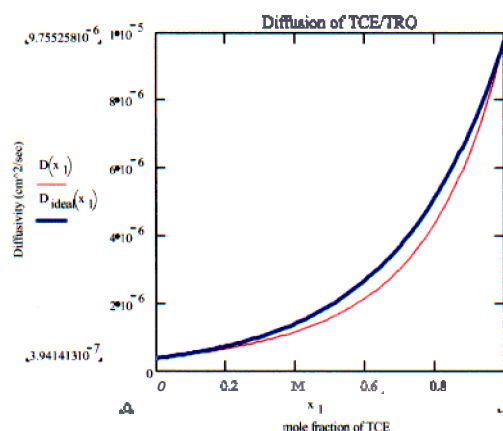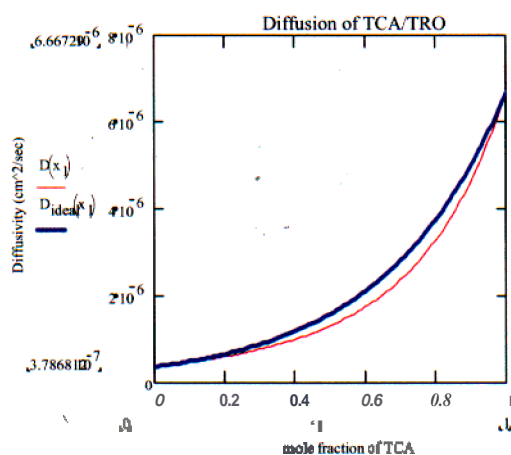Figure 4-28. Diffusion of 1,1,1-trichloroethane and Texaco Regal Oil using hexane and ideal behavior.

Figure 4-29. Diffiion of tetrachloroethene and Texaco Regal Oil using hexane and ideal behavior.

Figures 4-26 through 4-29 demonstrate an obvious difference between the modified Darken and Vignes equations. The modified Darken equation defines ideal diffusion as a linear function, whereas the Vignes equation defines ideal diffusion as an exponential function. Small decreases in the values of diffusion are seen when activity data for the chlorinated-hexane binary pairs are used in the thermodynamic correction factor. Analysis of these graphs reveals the same trends seen in Figures 4-22 through 4-25 (modified Darken)—use of activity data of the chlorinated solvent-hexane binary pairs as a substitute for solvent-TRO activity results in small decreases in the predicted diffusion coefficients for a given mole fraction.

An estimate of the effective diffusion coefficient for each binary pair was completed by taking an average value of the diffusion coefficient over the given range of mole fraction for the chlorinated solvent (0.9–0). Effective diffusion coefficients were calculated using both the modified Darken and Vignes equations. With each equation, activities of both the ideal mix and of the solvent-hexane binary pairs were used in the calculation of the thermodynamic correction factor. The results are listed in Table 4-3.

Table 4-3. Results of the empirical approach to estimating effective diffusion coefficients (cm^2/second).

Binary	Darken (hexane)	Darken (ideal)	Vignes (hexane)	Vignes (ideal)
Carbon tetrachloride and TRO	2.93E–6	3.34E–6	1.77E–6	2.03E–6
Trichloroethene and TRO	4.35E–6	5.12E–6	2.3OE-6	2.75E–6
1,1,1-trichloroethane and TRO	3.13E–6	3.57E–6	1.84E–6	2.10E–6
Tetrachloroethene and TRO	3.10E–6	3.69E–6	1.80E–6	2.12E–6

TRO = Texaco Regal Oil

Inspection of Table 4-3 reveals that the Darken equation consistently predicts values of the effective diffusion coefficient that are approximately 40% greater than those values generated by the Vignes equation. The use of activity data for the solvent-hexane binary pairs also consistently lowers the value of effective diffusion by approximately 12%. In both cases, TCE was predicted to have the highest rate of diffusion, and carbon tetrachloride was predicted to have the lowest rate of diffusion.

4.5   Discussion of the Empirical Methods

The use of chlorinated solvent-hexane activity data for the thermodynamic correction factor reveals only small decreases in the value of the diffusion coefficient as calculated by both the modified Darken and Vignes equations. In the thermodynamic section of this study, it has been shown that the liquid fraction of Series 743 sludge is either a quasi-ideal or ideal solution. Therefore, the thermodynamic correction factor would approach unity with use of the chlorinated solvent-TRO activity data. As a result, the diffusion coefficients would be linear or power functions of mole fractions (modified Darken or Vignes equations), suggesting that each solvent diffuses independently of any chemical interaction implied by deviations from ideality.

4.6   Results of the Fitted Analytical Solution to Petri Dish Data

The analytical solution of transient diffusion was fitted to the experimental data by adjusting the effective diffusion coefficient to minimize the least squared difference between the measured data and analytical solution. By means of minimizing this difference, the effective diffusion coefficient was fitted for each chlorinated solvent-TRO binary pair and for each solvent within the ternary mixture.

The analytical solution (shown in Equation 4-3) solves for the average remaining mass fraction of solvent left in the petri dish (Section 3, Equation 3-9):

$$\omega = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{\frac{-D \cdot (2 \cdot n+1)^2 \cdot \pi^2 t}{4 \cdot L^2}}$$

(4-3)

Through the use of a spreadsheet program, both the analytical solution and the experimental data were graphed as functions of time. The results of the fitting of the effective diffusion coefficient of the binary systems are graphically displayed in Figures 4-30 through 4-33. The heavy line is the observed experimental data.
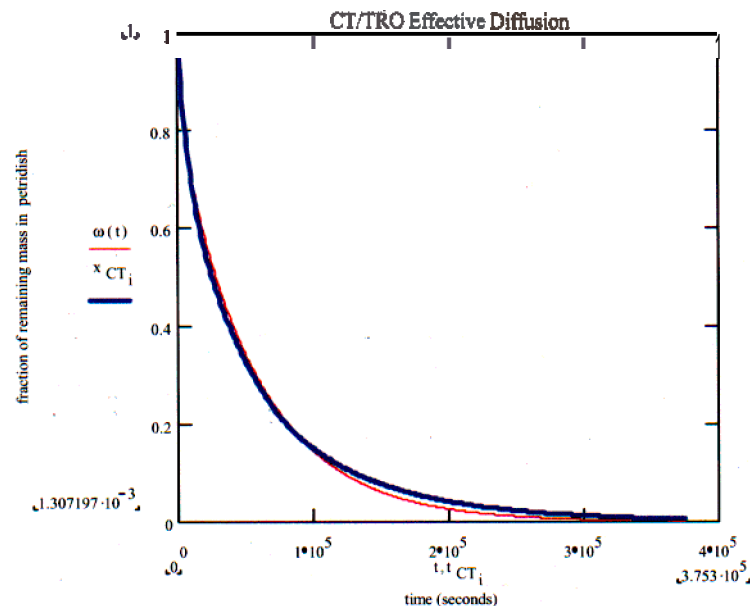
Figure 4-30. Fitting of the effective diffusion coefficient of carbon tetrachloride in Texaco Regal Oil.
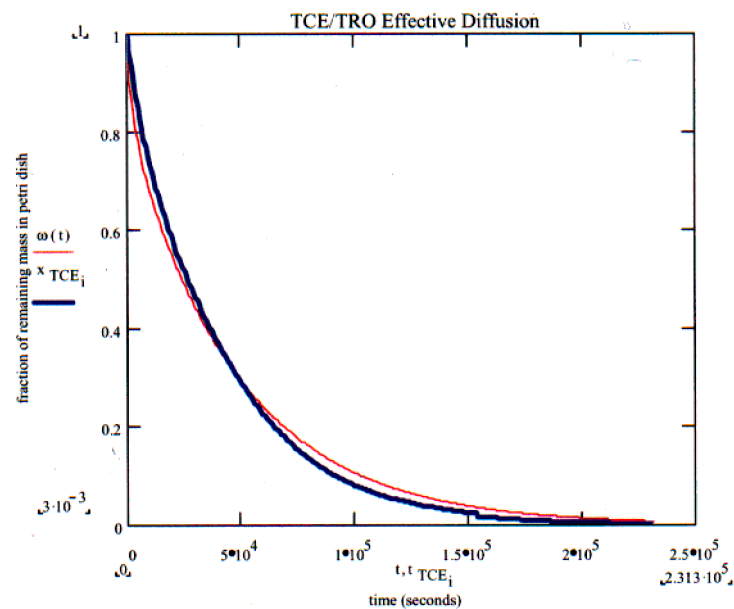
Figure 4-31. Fitting of the effective diffusion coefficient of trichloroethene in Texaco Regal Oil.
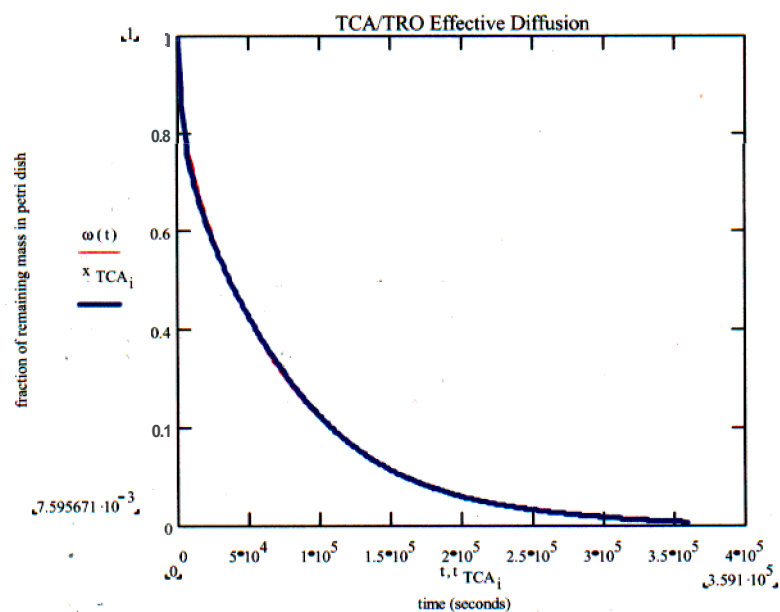
Figure 4-32. Fitting of the effective diffusion coefficient of 1,1,1-trichloroethane in Texaco Regal Oil.

4-13

PCE/TRO Effective Diffusion

fraction of remaining mass in petri dish

$\omega(t)$
$\times$ PCE$_i$

time (seconds)

Figure **4-33.** Fitting of the effective diffiion coefficient of tetrachloroethene in Texaco Regal Oil.

Table 4-4 summarizes the results derived from Figures 4-30 through 4-33 that include the value of the effective diffiion coefficient, the least squared difference, and the number of points considered in each graph.

Table 4-4. Results of analytical fit of the binary effective diffusion coefficients.

Solvent in Texaco Regal Oil	Effective Diffusivity (cm²/second)	Mean Squared Difference $-(\omega_{exp.} - \omega_{calc.})^2$/(number of data points)	Number of data pints
Carbon tetrachloride	5.50E–6	1.83E-4	418
Trichloroethene	6.80E–6	5.40E-4	257
1,1,1-trichloroethane	4.18E–6	3.05E-5	400
Tetrachloroethene	2.70E-6	2.05E-3	497

The use of the mean squared difference gives an indication of how well the experimental data are fitted with those numbers generated by the analytical solution of transient diffusion. The poorest fit is seen in the fitting of PCE with a mean squared difference of 2.05E–03. The square root of this number is the average difference between the experimental and analytical data, which is 0.045 or an average error of 4.5% (range of relative remaining mass fraction is 1.0–0). This small error for the most poorly fitted of the four effective diffusion coefficients indicates a reasonable fit of the data.

The analytical solution was also applied to the concentration data generated by the GC/MS analysis. The same method used in fitting the binary pairs was applied to the relative remaining mass fraction of each chlorinated solvent within the ternary mixture. The fitting of each chlorinated solvent within the ternary *mixture* is graphically demonstrated in Figures 4-34 through 4-37.
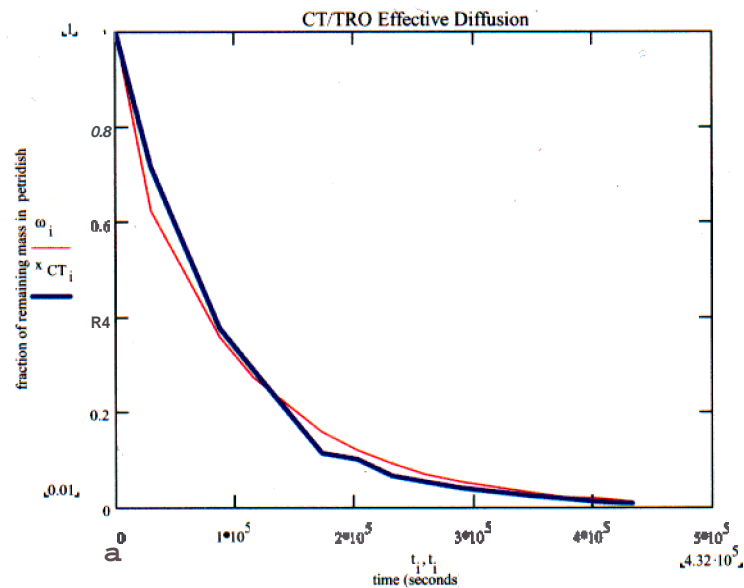
Figure 4-34. Fitting of the effective diffiion coefficient of carbon tetrachloride in the ternary *mix*.

Figure **4-35.** Fitting of the **effective diffusion coefficient of trichloroethene** in the ternary mix.

Figure 4-36. Fitting of the effective diffusion coefficient of 1,1,1-trichloroethane in the ternary *mix.*
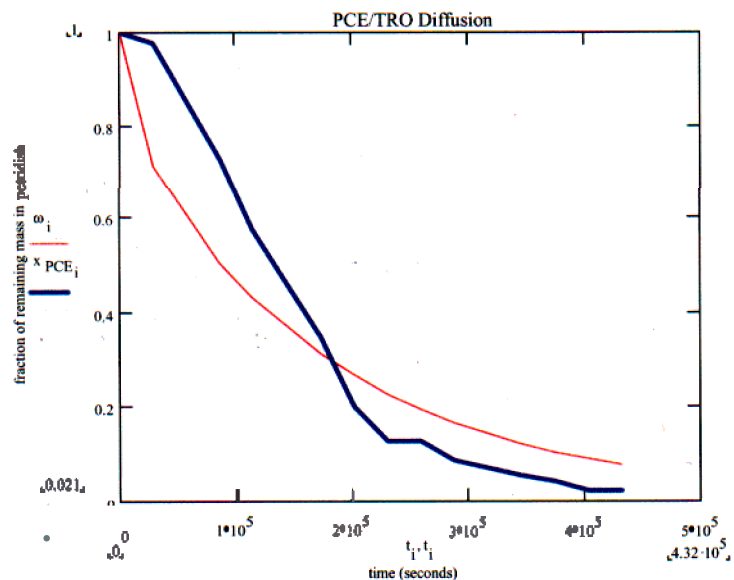
Figure 4-37. Fitting of the effective diffiion coefficient of tetrachloroethene in the ternary mix.

Table 4-5 summarizes the results from Figures 4-34 through 4-37. It includes the value of the effective diffusion coefficient, the least squared difference, and the number of pints considered in each graph.

4-16

Table 4-5. Results of analytical fit of the ternary effective diffusion coefficients.

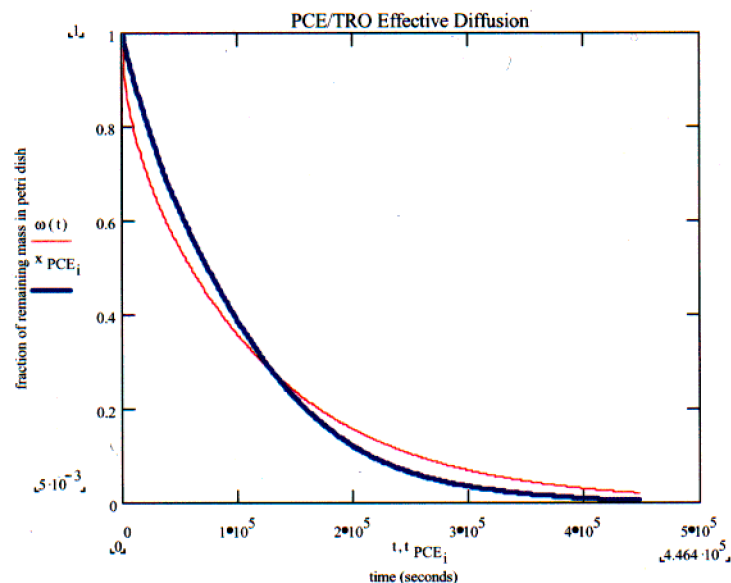| Solvent in Texaco Regal Oil	Effective Diffusivity (cm^2/second)	Mean Squared Difference $\sum(\omega_{exp} - \omega_{calc.})^2/(\text{number of data points})$	Number of data points
Carbon tetrachloride	3.085E–6	9.88E–4	13
Trichloroethene	3.67E–6	1.8lE–3	13
1,1,1-trichloroethane	3.06E–6	9.52E–4	13
Tetrachloroethene	1.80E–6	1.42E–2	13

Inspection of Table 4-5 reveals that the mean squared difference of the acquired ternary data is larger than that observed in the binary effective diffusion coefficient data (Table 4-4). The largest difference is seen with PCE with a mean squared difference of 1.42E–02. Taking the square root of this number reveals an average difference of 12%, a significant increase as compared to the binary result of 4.5%. The remaining three effective diffusion coefficients have a much smaller mean squared difference, indicating a reasonable fit given the small number of data points as compared to the binary data.

4.7   Discussion of the Analytical Solution of Transient Diffusion

Effective diffusion coefficients from the fit of the analytical solution to the binary and ternary data are compressed into Table 4-6.

Table 4-6. Comparison of binary and ternary values of effective diffusion.

Binary	Binary Effective Diffusion Coefficient (cm^2/second)	Ternary Effective Diffusion Coefficient (cm^2/second)
Carbon tetrachloride and TRO	5.5E–6	3.08E–6
Trichloroethene and TRO	6.8E–6	3.67E–6
1,1,1-trichloroethane and TRO	4.2E–6	3.06E–6
Tetrachloroethene and TRO	2.7E–6	1.80E–6
TRO = Texaco Regal Oil		

Because of resource limitations, the ternary experiment was run only one time. Despite this limitation, which may introduce some degree of error, the relative ratios effectively demonstrate similar rates of diffusion between the binary and ternary system.

It has been mentioned in this study that the effective diffusion coefficient is an average diffusion coefficient over a given range of concentration. One important factor that must be considered when discussing effective diffusion coefficients is that they are assumed to be constant over small ranges of concentration and are thereby independent functions of concentration (Taylor and Krishna 1993). In this study, the binary effective diffusion coefficient is used as an average diffusion coefficient over a significant range of concentration (mole fraction of 0–0.9). In the case of the ternary effective diffusion coefficients, the range of concentration is drastically reduced by a factor of four (0–0.225).

By considering the definition of an effective diffusion coefficient as an average diffusion coefficient over a given range, it can be argued that the reduction of the effective diffusion coefficient in the ternary system is the result of the drastic reduction in the concentration range as compared to the binary system. This statement is also supported by analysis of the variables found in the empirical equations used in this study. In each equation, the diffusion coefficient is dependent on two variables: mole fraction and thermodynamic correction factor. For ideal solutions, as in the case of the liquid fraction of Series 743 sludge, the thermodynamic correction factor is unity and drops out of both equations (modified Darken and Vignes). However, the calculation of effective diffusion coefficients is still dependent on the given range of mole fractions. When the concentration range is considered small, the effective diffusion coefficient can be assumed to be independent of concentration when considering mixtures that are within the given range. Given the proximity of the binary and ternary effective diffusion coefficients with the significant difference in the values of mole fraction, the results still vindicate the use of a the analytical solution of transient diffusion to predict effective diffusion coefficients.

4.8 Results of the Analytical Solution Applied to Open Canister Data

The analytical solution of transient diffusion was fitted to the experimental data obtained from the chlorinated solvent-TRO binary pairs in the aluminum canisters. The analytical solution was fitted by visual inspection to closely match with the experimental curve in the early time period of the experiment. The analytical solution (shown in Equation 4-4) solves for the average remaining mass fraction of the solvent left in the aluminum canister (Section **3,** Equation 3-5):

$$\omega = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} e^{\frac{-D \cdot (2 \cdot n+1)^2 \cdot \pi^2 \cdot t}{4 \cdot L^2}} \tag{4-4}$$

The experimental data were formatted to calculate the average remaining mass fraction of the chlorinated solvent in the aluminum canister. Using a spreadsheet program, both the analytical solution and the experimental data were graphed as functions of time. Results of the fitting of the effective diffusion coefficient of the binary systems are graphically displayed in Figures 4-38 through 4-41.
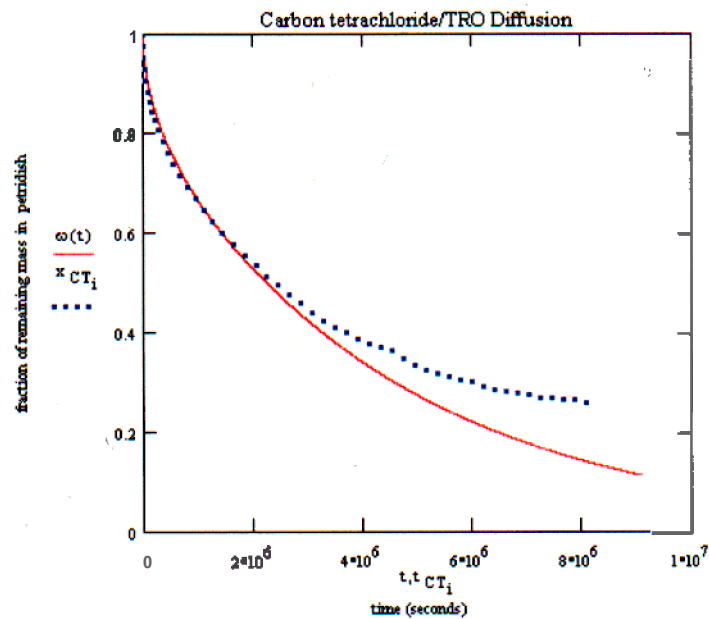
Figure 4-38. Fitting of the effective diffusion coefficient of carbon tetrachloride in Texaco Regal Oil.
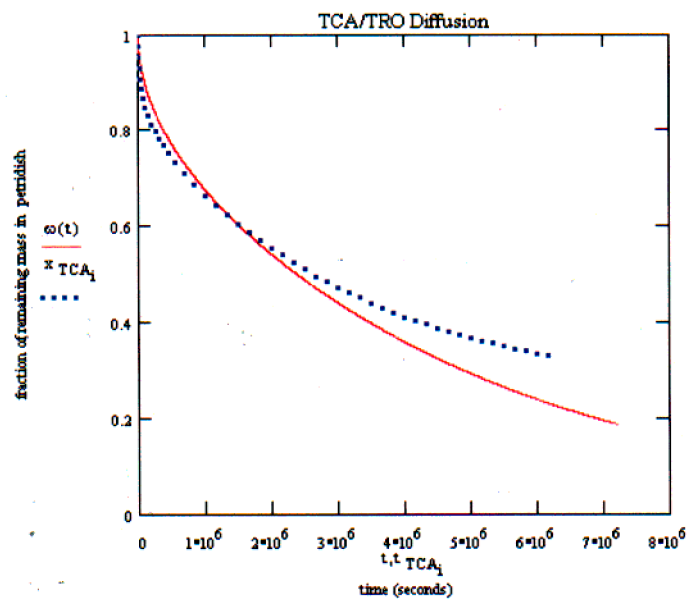
Figure 4-39. Fitting of the effective diffiion coefficient of 1,1,1-trichloroethane in Texaco Regal Oil,
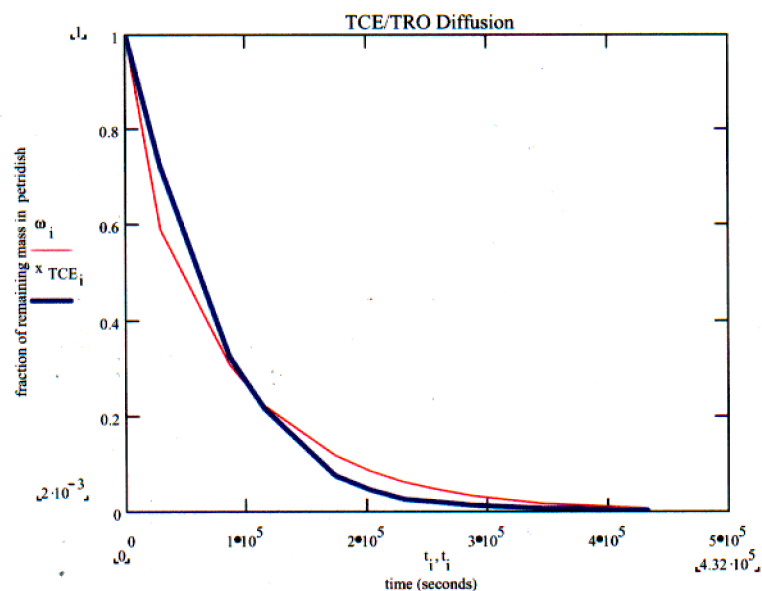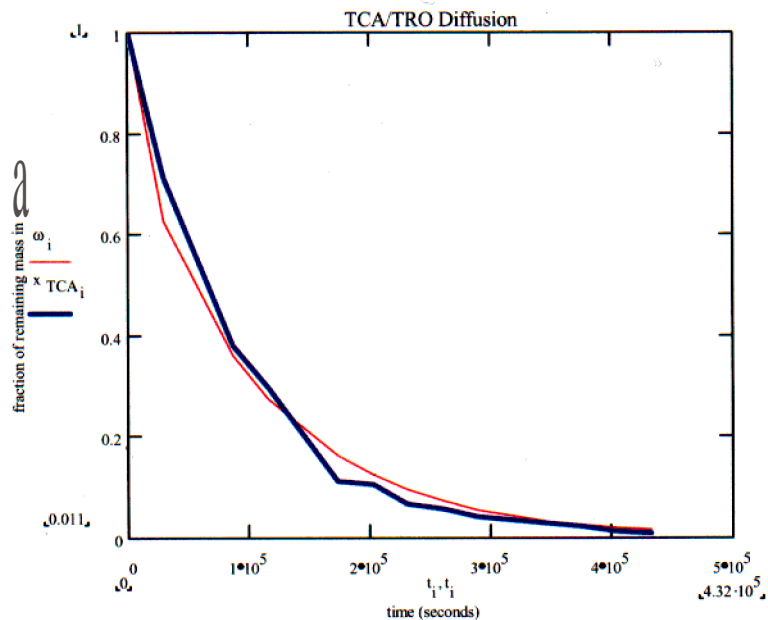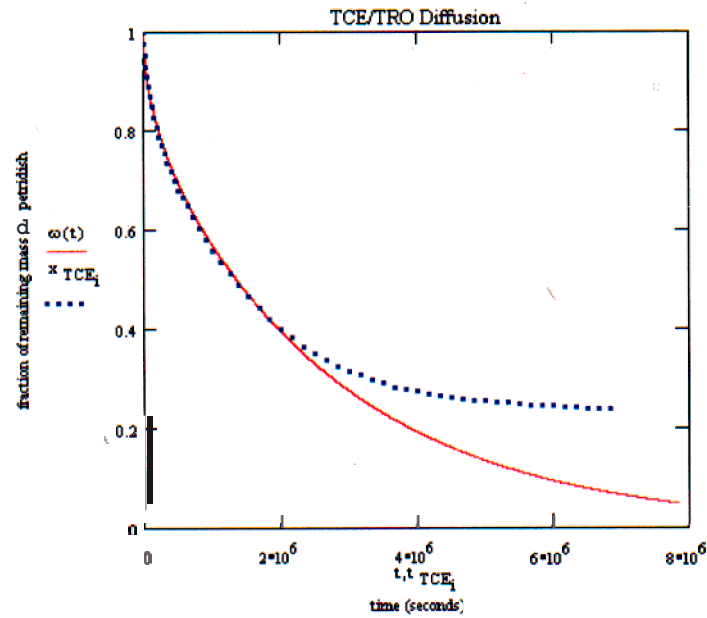
Figure 4-40. Fitting of the effective diffusion coefficient of trichloroethene in Texaco Regal Oil.
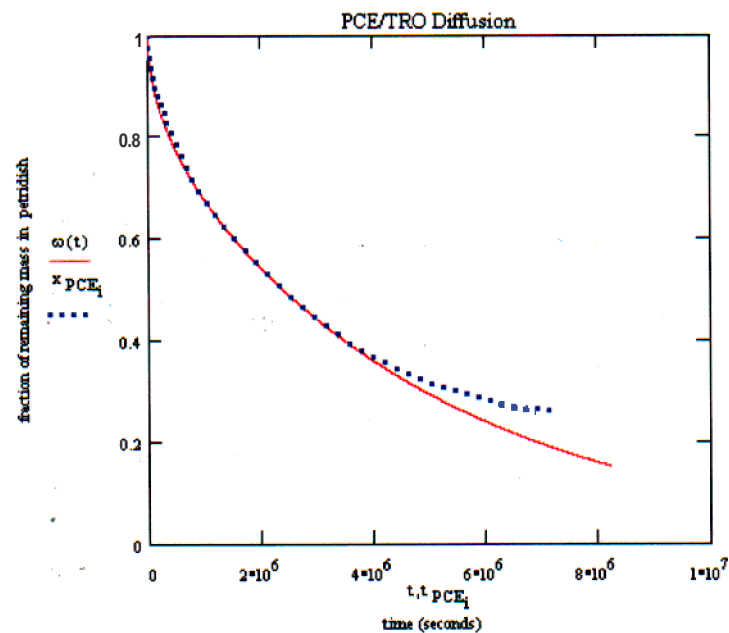
Figure 4-41. Fitting of the effective diffiion coefficient of tetrachloroethene in Texaco Regal Oil.

The effective diffusion coefficient calculated from the analytical solution for transient diffusion and the estimated period of time where the fitted curve best matches the experimental curve from the onset of the experiment are summarized in Table 4-7.

Table 4-7. Effective diffusion coefficient of binary pairs in an open aluminum canister

Binary	Binary Effective Diffusion Coefficient (cm^2/second)	Time of Best Matching of Curve (days)
Carbon tetrachloride and TRO	3.05E–6	23
Trichloroethene and TRO	5.05E–6	23
1,1,1-trichloroethane and TRO	3.5E–6	23
Tetrachloroethene and TRO	2.85E–6	46

TRO = Texaco Regal Oil

The solvent of PCE had the greatest length of time for curve matching between analytical solution and the experimental values, a value of 46 days. The other solvents appear to match best for the first 23 days.

A comparison of all four chlorinated solvent-TRO binary pairs in aluminum canisters without calcium silicate is graphically displayed in Figure 4-42. Chlorinated solvents, carbon tetrachloride and TCA, have the fastest rates of diffusion for the first 5 days of the experiment, and TCE has the fastest rate of diffusion for the remainder of the experiment. The PCE maintains the slowest rate of diffusion through oil of all the chlorinated solvents tested in open canisters.

The plot of remaining mass fraction levels off at approximately 0.2. It was assumed that no mass was lost in sample preparation. In retrospect, the initial mass could have been reduced by a factor of about 20% through evaporative loss in sample preparation.

Evaporation of sovlents in TRO in aluminum canisters
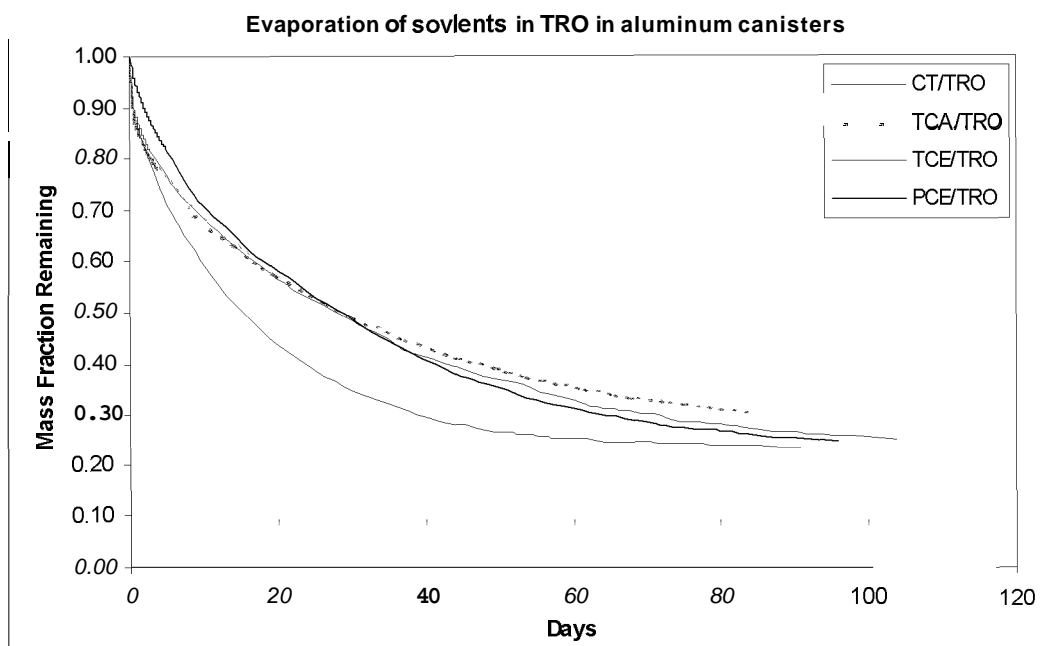
Figure 4-42. Comparison of each solvent and Texaco Regal Oil in an aluminum canister.

4.9 Discussion of the Analytical Solution of Transient Diffusion from an Open Canister

The results of the effective diffusion coefficients from Table 4-4 involving diffusion of chlorinated solvents through TRO in a petri dish and from Table 4-7 involving diffusion through TRO in an aluminum canister are combined in Table 4-8.

Table 4-8. Effective diffusion coefficients comparison of petri dish and aluminum can.

Binary	Effective Diffusion Coefficient (cm^2/second) Petri Dish	Effective Diffusion Coefficient (cm^2/second) Aluminum Canister
Carbon tetrachloride and TRO	5.50E–6	3.05E–6
Trichloroethene and TRO	6.80E–6	5.05E–6
1,1,1-trichloroethane and TRO	4.18E–6	3.5E–6
Tetrachloroethene and TRO	2.70E–6	2.85E–6
TRO = Texaco Regal Oil		

Comparing the effective diffusion coefficients from two geometric configurations, the petri dish and aluminum canister, shows that the effective diffusion coefficients for the aluminum canisters are smaller in general but are within the order of magnitude determined for the petri dish experiments.

The differences of fit of the analytical solution with the aluminum canisters could be because of the stagnant head space above the surface of the chlorinated solvent and TRO. The head space above the mixture increased as the volume in the canister decreased. As head space increased, the walls of the aluminum canister prevented any air circulation that would normally evacuate diffused solvent from the fluid surface in a petri dish configuration. Because of this, the relative mass loss decreased (compared with that from open petri dish), and the fitted diffusion coefficient was somewhat lower. This is shown in Figures 4-3**8** through 4-41.

Although curve fitting of the analytical solution with data from the aluminum canisters does not match entirely through the duration of the experiment, it suggests that the effective diffusion coefficient, estimated by gravimetric analysis, is independent of the physical configuration.

4.10 Results of Mass Loss of Solvents Mixed with Calcium Silicate from an Open Canister

The analytical solution for transient diffusion was developed for heat diffusion in solids and is commonly applied to liquid/liquid diffusion. Here, the presence of calcium silicate introduces solidliquid interactions that are not accounted for in the solution. Because of this, a graphical comparison was made first of the chlorinated solvent-TRO binary pairs mixed with and without calcium silicate contained in a canister. After this, an estimate of the effective diffusion was made by applying the analytical solution of transient diffusion and is employed here to illustrate the effect of the solidliquid interactions introduced by the calcium silicate on solvent diffusion.

In the Figures 4-43 through 4-46, each chlorinated solvent-TRO binary pair is compared graphically with and without calcium silicate.
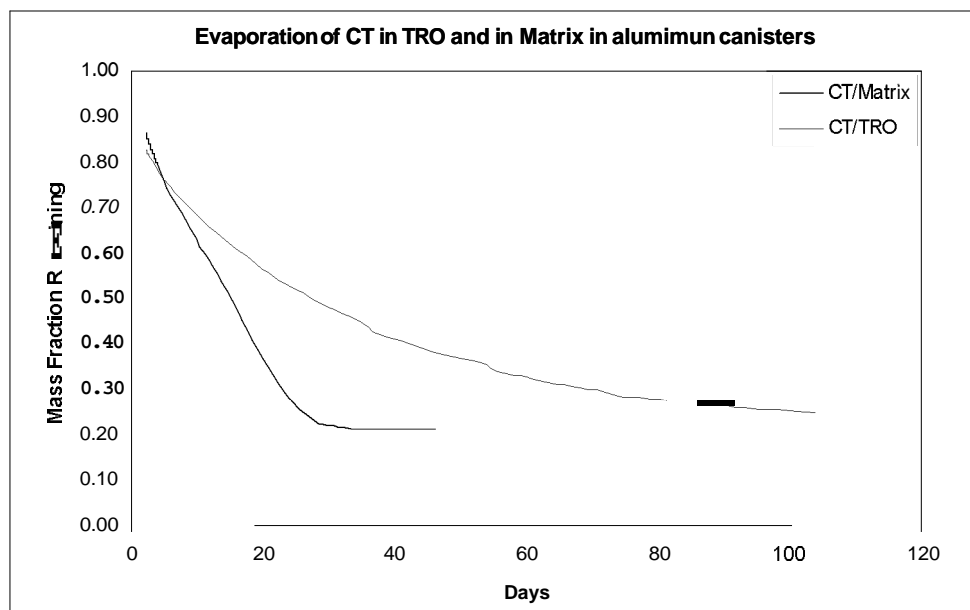
Figure 4-43. Comparison of the evaporation effects of carbon tetrachloride in Texaco Regal Oil and calcium silicate.

Evaporation of TCA in TRO and in Matrix in aluminum canisters
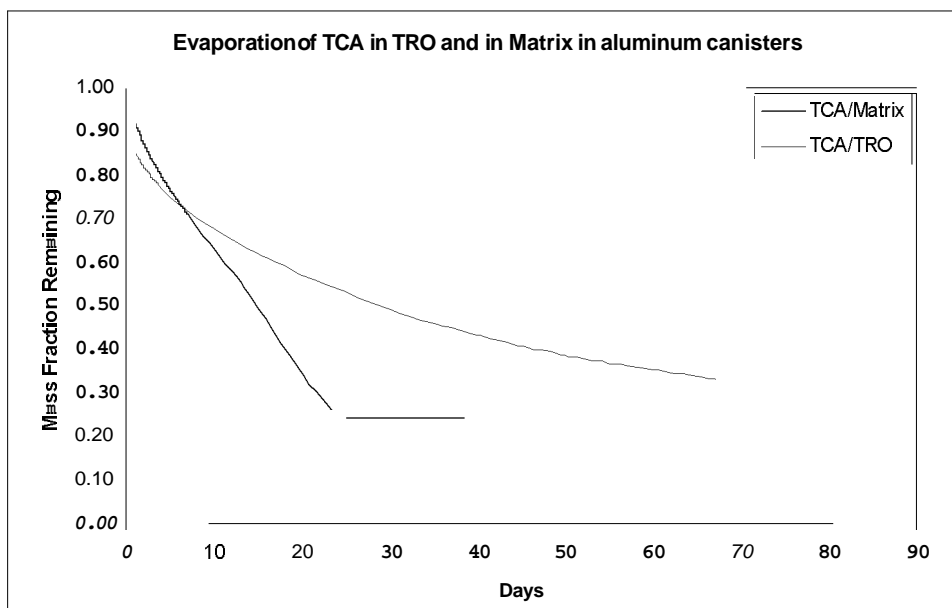
Figure 4-44. Comparison of the evaporation effects of 1,1,1-trichloroethane in Texaco Regal Oil and calcium silicate.

Initially, the solvents carbon tetrachloride and TCA had a faster rate of mass loss through TRO than through calcium silicate: 6 days for carbon tetrachloride and 10 days for TCA. Both solvents diffused slower in TRO for the remainder of the experiment (see Figures 4-43 and 4-44).

Figure 4-45 shows that TCE also displayed quicker diffusion through TRO than through calcium silicate, though it was not until 12 days before that the rate of mass loss was more rapid in calcium silicate than through TRO.

Evaporation of TCE in TRO and in Matrix in aluminum canisters
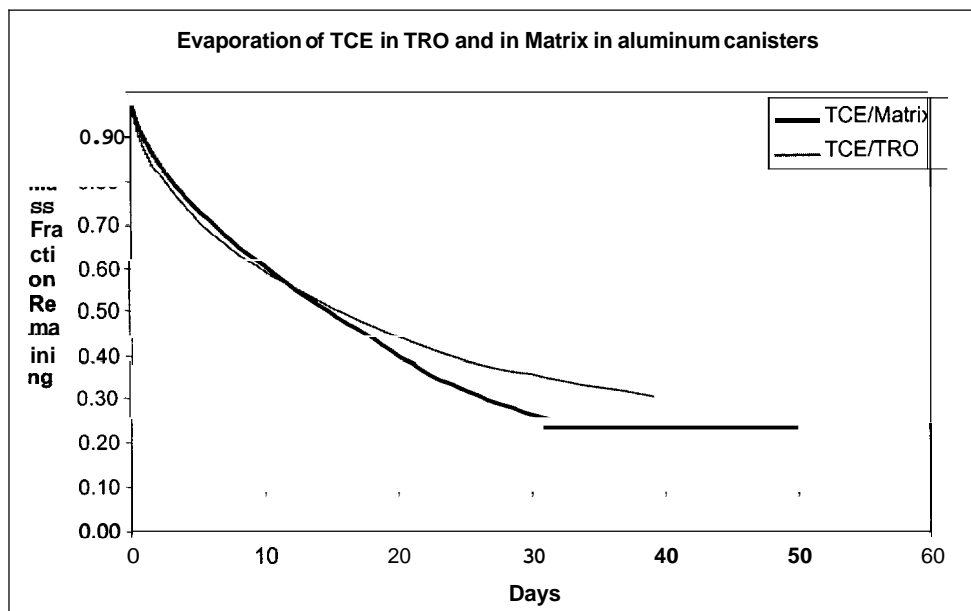
Figure 4-45. Comparison of the evaporation effects of trichloroethene in Texaco Regal Oil and calcium silicate.

A comparison of PCE diffusion in TRO and calcium silicate (Figure **4-46**) shows a similar trend as that of the previous solvents; however, it is not until about Day 84 that diffusion was observed to be faster through calcium silicate than through TRO. This was much later than for carbon tetrachloride, TCA, and TCE. We have not carefully examined reasons for the late crossover, but we suspect that molecular size or chemical properties may have contributed to this observation.

Evaporation of PCE in TRO and in Matrix in aluminum canisters
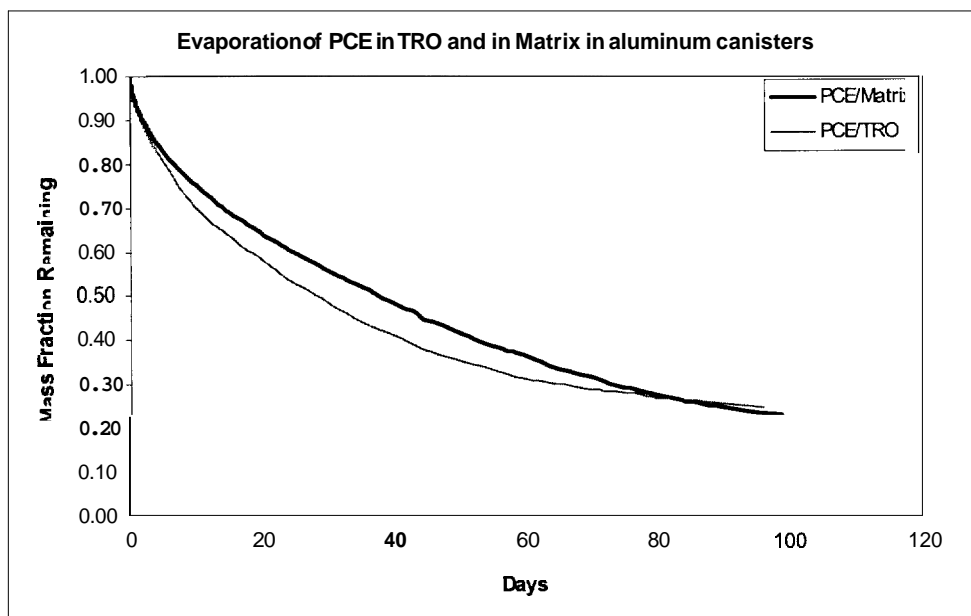
Figure 4-46. Comparison of the evaporation effects of tetrachloroethene in Texaco Regal Oil and calcium silicate.

Curve-fitting the analytical solution to estimate an effective diffiion coefficient for the solvent-TRO mixture in calcium silicate provided values that are within the order of magnitude of the values obtained from the petri dish and aluminum canister experiments without calcium silicate (see Table 4-9).

Table 4-9. Effective diffusion coefficients of petri dish and aluminum can without matrix.

Solvent in Texaco Regal Oil	Effective Diffusion Coefficient $(cm^2/second)$ Petri Dish	Effective Diffusion Coefficient $(cm^2/second)$ Aluminum Can	Effective Diffusion Coefficient $(cm^2/second)$ Aluminum Can with Calcium Silicate
Carbontetrachloride	5.50E–6	3.05E–6	2.50E–6
1,1,1-trichloroethane	6.80E–6	5.05E–6	4.05E–6
Trichloroethene	4.18E–6	3.50E–6	5.52E–6
Tetrachloroethene	2.70E–6	2.85E–6	2.02E-6

Comparison of solvent mass loss curves in TRO and a calcium silicate matrix with values from the analytical solution of transient diffusion do not match well with carbon tetrachloride and TCA, suggesting that, as expected, a mechanism other than diffusion alone was involved in the mass loss. This mechanism appears to increase the rate of transportation through the solid matrix (Figures 4-47 and 4-48).

The TCE and PCE data appear to better fit a diffusion model, but after a few days, mass loss is also observed to exceed a diffusive prediction (Figures 4-49 and 4-50).
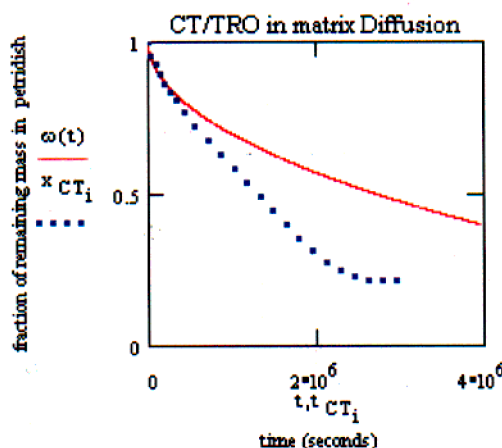
Figure 4-47. Fitting of the effective diffision coefficient of carbon tetrachloride and Texaco Regal Oil in matrix.
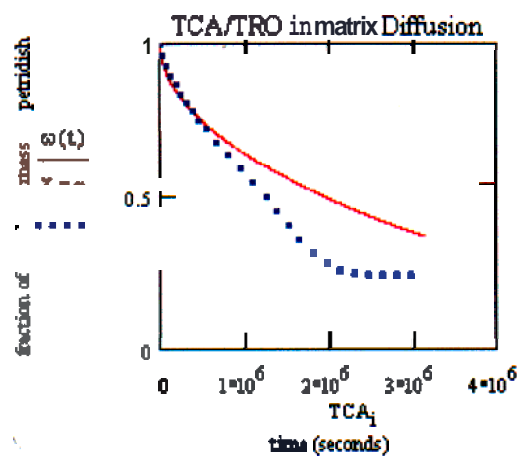
Figure 4-48. Fitting of the affective diffusion coefficient of 1,1,1-trichloroethane and Texaco Regal Oil in matrix.
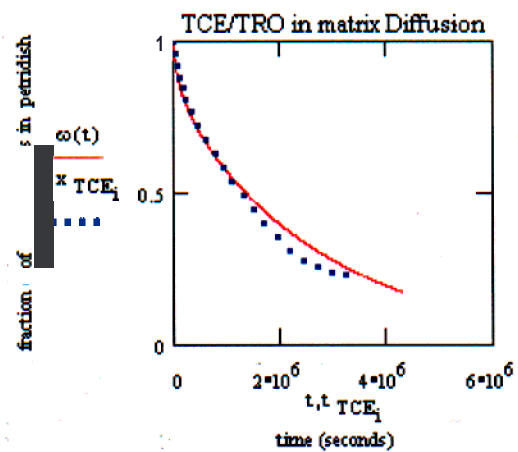
Figure 4-49. Fitting of the effective diffusion coefficient of trichloroethene and Texaco Regal Oil in matrix.
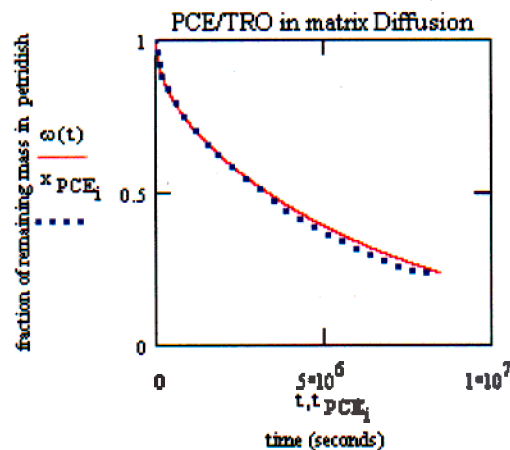
Figure 4-50. Fitting of the effective diffusion coefficient of tetrachloroethene and Texaco Regal Oil in matrix.

A comparison of the four chlorinated solvents, TRO binary pairs in aluminum canisters with calcium silicate is graphically displayed in Figure 4-51. The rate of mass loss through TRO with calcium silicate for carbon tetrachloride, TCA, and TCE was completed within approximately 29, 24, and 33 days, respectively, while PCE required approximately 100 days.
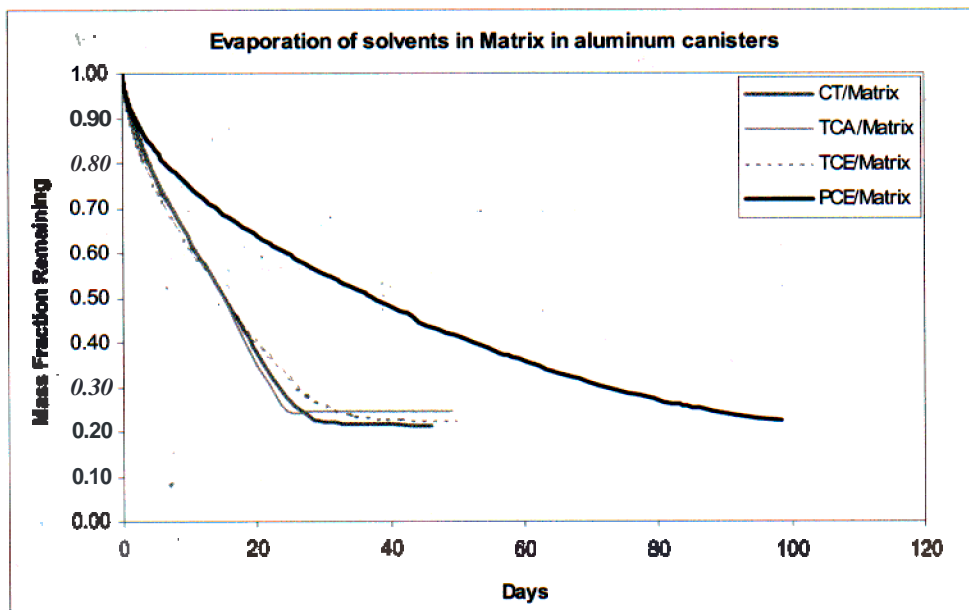
Figure 4-51. Comparison of evaporation effects of all solvent and Texaco Regal Oil in calcium silicate.

4.11 Discussion of the Rate of Mass Loss from Calcium Silicate In an Open Canister

The solvent mixtures of carbon tetrachloride, TCA, and TCE in TRO with calcium silicate were observed to diffie more quickly after Day 6 for carbon tetrachloride, Day 10 for TCA, and Day 12 for TCE than mixtures without calcium silicate (Figures 4-42 through 4-44). There appeared to be some

shrinkage of matrix from the sides of the canister. This was detected after the experiment when the canister could be gently shaken, and slight movement of the dried calcium silicate could be experienced. This could increase surface area for lateral diffusion to take place and allow for more rapid solvent escape.

Also, the calcium silicate was not completely dry because it retained the TRO. As the solvent evacuated the matrix, there may have been physical micropathways left behind, thereby facilitating migration of the solvent through less TRO before it reached the matrix-air interface for escape.

Interestingly, unlike the chlorinated solvents carbon tetrachloride, TCA, and TCE, PCE diffused faster in the oil than in the calcium silicate matrix. It was not until approximately 80 days into the experiment when PCE diffused faster in the matrix (See Figure 4-45). Perhaps the molecular structure of PCE affects the rate of diffusion through the calcium silicate. The PCE has four chlorine atoms attached to the ethylene backbone, making the molecule larger in size than the other solvents. The presence of the double bond makes the molecule rigid, thereby restricting the molecule from rotating around the carbon atoms. This leaves PCE to one confirmation only. Combining these two factors could slow the molecule's migration through the rigid pathways formed by the TRO-calcium silicate mixture. However, in TRO only, the medium is in constant flux, facilitating PCE tumbling through the oil.

Carbon tetrachloride is symmetrical like PCE but is configured in a tetrahedron shape, making it smaller in size than PCE. Because of this, it may be able to move through the rigid pathways easier than PCE. The TCA is similar to PCE but has one less chlorine atom (smaller in size) and a single bond between carbon atoms. This can allow for rotation and multiple confirmations or twisting movements through the matrix. The TCE is very similar in configuration to PCE with the rigid double bond but contains one less chlorine atom, making it smaller. Perhaps the extra chlorine in PCE is the restricting factor in this migration through calcium silicate. More investigation must be done concerning the stereochemistry of the solvents and the interaction or diffusion through the calcium silicate matrix.

4.12 Results of Mass Loss from a Sealed Canister with an Escape Hole

Experiments involving mixtures of binary chlorinated solvent and TRO mixed with calcium silicate and placed in a sealed aluminum canister with a single-sized hole (e.g., 1/4 in., 1/8 in., or 1/16 in.) are graphically represented in Figure 4-52. The canisters with the largest hole (1/4 in.) had the greatest rate of mass fractional loss of chlorinated solvent over time. As might be expected, the canisters with a hole size of 1/8 in. were next, followed by the canisters with a hole size of 1/16 in.

Evaporation of Matrix /Field Mix in Drum with various hole sizes
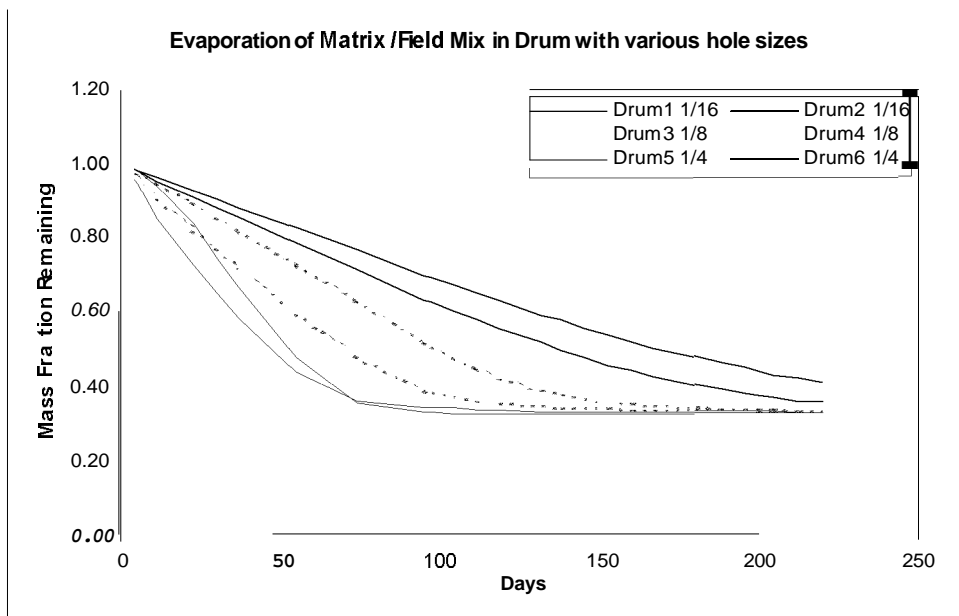
Figure 4-52. Comparison of single-hole sizes in sealed canister filled with sludge.

The experiment was repeated with similar results shown in Figure 4-53. Again, the canisters with a 1/4-in. hole displayed the greatest rate of mass fractional loss of chlorinated solvent over time. This was followed by canisters with hole sizes of 1/8 in. and 1/16 in., respectively. Note that in each set of canisters done in duplicate, there was some variability in the rate of escape. Table 4-10 shows the escape time as a function of hole size.

Table 4-10. Escape time as a function of hole size.

Hole Size (in.)	Escape Time (days)
1/4	80
1/8	160
1/16	230

The mass fraction remaining was exhausted at about a fraction of 0.32 in tlns experiment.

Evaporation of Matric/CT in Drums with **varied Hole sizes**

Legend:
Drum A 1/16   Drum B 1/16
Drum C 1/8   Drum D 1/8
Drum E 1/4   Drum F 1/4

Y-axis: Mass Fraction Remaining
X-axis: Days
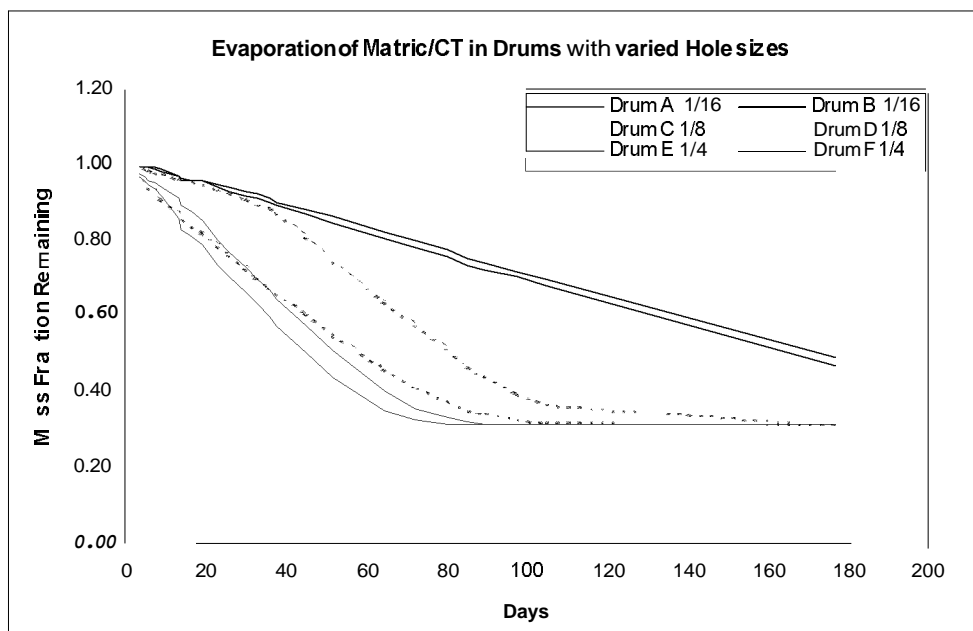
Figure 4-53. Comparison of single-hole sizes in sealed canister with sludge.

Insertion of a hole into a sealed canister may be scaled up to estimate the fractional mass loss through a corroded hole in a 55-gal drum. Each hole size (e.g., 1/4 in., 1/8 in., or 1/16 in.) represents a percentage of surface area of corrosion in a 55-gal drum. A hole size of 1/4 in. represents an area of corrosion of 3.1 in. in diameter (see Table 4-11). Similarly, a hole size of 1/8 in. corresponds to a corroded hole with a diameter of 1.55 in., and a hole size of 1/16 in. corresponds to a hole with a diameter of 0.77 in. Following the linear scale-up reasoning, a similar timeframe might be expected for escape of carbon tetrachloride from a 55-gal drum with comparable-sized corrosion holes (see Table 4-11).

Table 4-11. Corresponding sized holes between an aluminum canister and a 55-gal drum.

Hole-Size Diameter (in.)	Surface Area of Hole (cm^2)	Percent of Aluminum Can Surface Area 129.3 (cm^2)	Hole Surface Area of 55-gal Drum 19792 (cm^2)	Hole-Size Diameter in 55-gal Drum (in.)
1/4	0.317	0.245	48.49	3.10
1/8	0.0792	0.061	12.13	1.55
1/16	0.0198	0.015	3.03	0.77

4.13 Discussion of Mass Loss from a Sealed Canister with an Escape Hole

The importance of a single escape hole in the canister shows how quickly chlorinated solvents can escape from the canister. As the hole size increases from 1/16 in. to 1/8 in. and then to 1/4 in., the time for solvent escape is approximately 239 days, 160 days, and then 80 days, respectively.

However, unlike laboratory conditions, there are other variables that influence the rate of solvent escape from drums in the field. This makes it difficult to estimate or determine times for solvent escape from drums under field conditions. The following realistic variables might affect these rates in the field:

- Corrosion holes will initially develop as pinholes in drums and grow over time. The time of formation of the first pin-sized holes is unknown as is their rate of enlargement. The time before VOC escape is unknown and is probably variable from location to location within the SDA. Also: the rate of escape will vary over time with the hole diameter.

- The solvent-to-sludge ratio actually used at the Rocky Flats Plant may vary within the approximately 10,000 drums buried at the SDA. The rate of VOC migration will vary with the solvent-to-sludge ratio.

Depending upon the above-mentioned variables, it appears that it takes a few years for diffusive transport and migration through corrosion holes in drums. The influence of plastic bagging around the sludge is also an important component of the potential escape of VOCs from the sludge matrix and is subsequently discussed.

4.14 Discussion of Volatile Organic Compound Permeability through Plastic Bagging Containing Sludge

Having previously discussed the rate of mass loss of VOCs from oil-and-calcium silicate in open canisters and from sealed canisters with a single hole, it is important to discuss a third parameter preventing VOC escape, that being the plastic bagging surrounding the sludge. Liekhus and Peterson (1995) reported permeability values for VOCs escaping through polymer bags. These bags are similar to or are the bags used to store sludge at the SDA site in Idaho. Liekhus and Peterson (1995) report that VOC permeability values through polyethylene bagging are in the order of 10^{-10} cm^3 (standard temperature and pressure) cm^{-1} s^{-1} (cm mercury [Hg])$^{-1}$ for carbon tetrachloride, TCA, and TCE (see Table 4-12).

Table 4-12. Permeability values of the volatile organic compounds carbon tetrachloride, 1,1,1-trichloroethane, and trichloroethene through polyethylene bagging (Liekhus and Peterson 1995).

	Carbon Tetrachloride	1, 1, 1-Trichloroethane	Trichloroethene
Permeability cm^3 (STP) cm^{-1} s^{-1} (cm Hg)$^{-1}$	181E–10	118E–10	496E–10

Units assigned to permeability values are cm^3 (STP) cm^{-1} s^{-1} (cm Hg)$^{-1}$. The volumetric loss rate of VOCs escaping through the bagging can be calculated by multiplying its permeability value by surface area of exposed bagging and by its vapor mole fraction and then dividing by the bagging thickness (shown in Equation 4-5):

$$p, x \ (y_i \ x \ P) \ x \ SA/th = cm^3/second \tag{4-5}$$

where

y_i = vapor mole fraction of ith VOC in vapor phase (cm' VOC/ cm^3 gas)

P = pressure surrounding vapor (cm Hg)

SA = surface area of the bagging (cm^2)

th = thickness of the bagging (cm)

p_i = permeability of ith VOC (cm' (STP) cm^{-1} s^{-1} (cm Hg)$^{-1}$).

Note the utility of these unusual units:

$$\left(\frac{cm^3}{cm \cdot s \cdot cm\,\mathrm{Hg}}\right)\left(\frac{cm^3\,\mathrm{voc}}{cm^3\,\mathrm{gas}}\right)\left(\frac{cm\,\mathrm{Hg}}{1}\right)\left(\frac{cm^2}{1}\right)\left(\frac{1}{cm}\right)=\frac{cm^3}{s}\quad.$$

The permeability values used in this calculation are based upon a single VOC diffusing across a polyethylene bag. Liekhus and Peterson (1995) determined that VOC permeability through polymer bagging at 25°C was not affected by the presence of other VOCs in the gas mixture. A similar conclusion was also observed in this report with regards to VOCs diffusing through TRO oil. That is, VOC diffusivity through oil is not affected by the presence of other VOCs in the liquid mixture. Because of this, permeability values obtained for single VOCs will be used for calculating total volume loss.

The VOC permeability p_i values, determined by Liekhus and Peterson (1995), were determined using vapor mole fraction y_i values derived from concentrations that are much lower than values determined to be within the drums buried at the INEEL Site in Idaho. The concentrations ranged from 0.2 mg/L to 7 mg/L, whereas concentrations determined in the drums onsite are 5 mg/L to 371 mg/L. The permeability values determined by Liekhus and Peterson (1995) for calculating VOCs remaining in the buried drums will be conservative at best; the rate of volume diffusing across the bagging will be underestimated.

The y_i vapor mole fraction of VOCs drives the VOC migration across the polyethylene bagging; however, this vapor fraction does not remain constant throughout the life of storage. As VOCs escape through the polyethylene bag, vapor mole fractions of VOCs inside the bagging are subject to change, thereby affecting the rate of each VOC permeating through the bagging.

Three VOCs, which include carbon tetrachloride, TCA, and TCE, diffuse through the silicate matrix at similar rates. Carbon tetrachloride was the quickest to diffuse through the matrix, taking approximately 26 days, followed by TCA, taking 30 days, and TCE, taking 32 days. The PCE had taken as long as 100 days. The vapor composition within the bagged sludge determined from this report is approximately 88.4% carbon tetrachloride, 7.5% TCE, 3% TCA, and 1% PCE. The highest percentage of vapor fraction is carbon tetrachloride, suggesting that VOCs escaping through the polyethylene bag are primarily a one-component system. Because of this, it is assumed that the change in y_i vapor mole fractions will not be affected dramatically until there are insufficient VOCs within the bagged material to maintain the ratio. Until then, the time for solvent escape, primarily carbon tetrachloride, through the polyethylene bag can be estimated.

Unofficial reports from the INEEL suggest that 37 gal of liquid make up the sludge contents in a 55-gal drum. Of the 37 gal, approximately 24.7 gal consist of VOCs, and 12.3 gal consist of TRO. It is

assumed, because of the lack of evaporation of TRO from experiments, that TRO does not contribute to a vapor fraction and is not included in the overall calculation of liquid escaping from the storage drum. Therefore, the target of 24.7 gal was used to determine when all the VOCs have escaped through the polyethylene bag. The time for complete VOC release from the polyethylene bag is estimated for two drum positions standing vertical and lying on its side. When the drum is in a vertical position, it is estimated to take 65.75 years for VOCs to completely escape from the bagging, and when it is on its side, only 35.21 years are estimated (see Table 4-13). A conceptual diagram and calculations are found in Appendix C. Escape from corroded holes in the head space of the drums is considered to happen more quickly than diffusion across the polyethylene bagging.

Table 4-13. Estimated time for complete escape of volatile organic compounds from polyethylene bag.

	Surface Area (cm^2)	Time to Completely Escape (years)
Vertical	2,451	65.75
Horizontal	4,575	35.21

When the drum is in a vertical position, it is assumed that permeating VOCs are restricted to the top of the bagged sludge. This is caused by the weight of the sludge material pressing against the side and bottom of the drum, reducing vapor space relative to the top of the sludge and bag. Similarly, as the drum is placed on its side, there is more vapor space at the top surface of the bagged sludge than along the sides of contact with the drum wall. The increased surface area created while the drum is in the horizontal position contributes to more total VOC escape, decreasing the time required for complete diffusion.

As VOCs escape over time, there is a depletion of total VOCs inside the bagging required to replenish the vapor fractions. As this occurs, the driving influence of the vapor fraction (y_i) would be expected to decrease, and the length of time for the VOCs to escape would be expected increase.

From the results in this report, comparison of VOC vapor escape from polyethylene bags and VOCs escaping from open and sealed canisters with holes suggests that the limiting parameter of VOC escape is the polyethylene bagging. Considering this, if the integrity of the drums was compromised in any way, like corrosion, VOC vapor between the drum wall and bagging would quickly escape. This escape would be the driving force necessary for VOCs from the sludge to permeate through the polyethylene bag to reestablish an equilibrium concentration. However, because of vapor escaping the drum, the vapor concentration would not reach equilibrium and would eventually allow most, if not all, VOCs to escape storage and be released into the vadose zone.

5.   SUMMARY AND CONCLUSIONS

5.1   Summary

5.1.1   Activity Coefficient Analysis

Literature data from the DECHEMA database, in conjunction with some estimated data from UNIFAC, were used to predict the cumulative chemical interactions between the four chlorinated solvents and TRO in terms of activity coefficients. Literature data using hexane as the solvent in place of TRO with the solvents demonstrate that the four chlorinated solvent-hexane binary pairs are near ideal mixtures. The UNIFAC estimates of activity coefficients for the solvent-TRO binary pairs suggest negative deviations for three of the four binary pairs. Both the DECHEMA and UNIFAC data are supported by a classification that binary mixtures of these chlorinated solvents (carbon tetrachloride, TCE, TCA, and PCE) with hydrocarbons (hexane and TRO) are either quasi-ideal or ideal.

Close observation of the experimental activity coefficients of the chlorinated solvents-hexane binary pairs show that the resulting curves are almost identical to each other in shape and size. Extrapolation of this observation implies that the four chlorinated solvents interact with hexane in a similar fashion. Based upon this observation, it can be argued that since hexane and TRO are both saturated hydrocarbons with no polar functional groups, the activity curves for the solvent-TRO binary pairs should also be near identical.

Contained within the DECHEMA database are additional experimental data for a variety of carbon tetrachloride, alkane binary pairs. Two general trends are noted with both the increasing chain length and increasing degree of branching. Activity approached ideality, particularly with the carbon tetrachloride, octane binary, but began to show small negative deviations with increasing carbon chain length. The second trend suggests that although increased alkane branching slightly increased the activity coefficient, increasing the length of these branched compounds still decreased the overall activity.

Analysis of the six solvent/solvent binary pairs revealed that, in all cases, very little deviation from ideality was seen in any particular binary. Literature data for four of the six binary pairs (carbon tetrachloride and TCE, carbon tetrachloride and TCA, carbon tetrachloride and PCE, and TCE and PCE) revealed no notable deviations in the activity coefficient. The UNIFAC equation was used to predict the activity coefficients for the remaining TCA-TCE and TCA-PCE binary pairs. The results showed some positive deviations for the TCA-TCE binary and negative deviations for TCA and PCE but were still small enough to consider the two binary pairs as ideal solutions.

5.1.2   Empirical Approach

Effective diffusion coefficients were calculated using both the modified Darken and Vignes equations. Each equation required the input of infinitely dilute diffusion coefficients calculated by the Wilke-Chang equation. Both the modified Darken and Vignes equations account for nonideal mixtures through the use of the thermodynamic correction factor. Two approaches were used for the correction factor. In the first approach, the activity data for each chlorinated solvent-hexane binary pair were used as a proxy for solvent-TRO activity to calculate effective diffusion coefficients for each solvent-TRO binary pair. In the second approach, each binary pair was considered to be an ideal mixture, and a thermodynamic correction factor of unity was used. Use of the solvent-hexane thermodynamic correction factor in both the modified Darken and Vignes equations for each solvent-TRO binary pair resulted in slightly lower predicted effective diffusion coefficients.

5.1.3 Analytical Approach

A series of petri dish experiments using an automated gravimetric system was used to collect data for application of an analytical solution solving for effective diffusion coefficients.

Effective diffusion coefficients for each set of experiments were fitted using the least mean squared difference method. The value of the effective diffusion coefficient was adjusted until the mean squared difference between the experimental data and the analytical solution was minimized.

The results of the application of the analytical solution were a set of four distinct effective diffusion coefficients for both the binary and ternary mixtures. Results of the analytical solution are slightly larger than those predicted by the modified Darken and Vignes equations and are compared in Table 5-1.

Table 5-1. Results of the three methods of finding effective diffusion coefficients.

Binary	Analytical Solution (cm^2/second)	Modified Darken (cm^2/second)	Vignes (cm^2/second)
Carbon tetrachloride and TRO	5.5E–6	3.34E–6	2.03E–6
Trichloroethene and TRO	6.8E–6	5.12E–6	2.75E–6
1,1,1-trichloroethane and TRO	4.1E–6	3.57E–6	2.10E–6
Tetrachloroethene and TRO	2.7E–6	3.69E–6	2.12E–6

TRO = Texaco Regal Oil

As can be seen in Table 5-1, the values of both the empirical approach and analytical solution fall within an order of magnitude, suggesting that this is the appropriate range for these effective diffusion coefficients. Another observation supporting the results of the analytical solution is effectively demonstrated by showing how the resulting effective diffusion coefficients fall in between the infinitely dilute diffusion coefficients calculated by the Wilke-Change method as seen in Table 5-2.

Table 5-2. Placement of analytical diffusion value in the ranges of infinite dilution.

	Carbon Tetrachloride (cm^2/second)	Trichloroethene (cm^2/second)	1,1,1-Trichloroethane (cm^2/second)	Tetrachloroethene (cm^2/second)
Solvent in TRO Diffusion	3.93E–7	3.94E–7	3.79E–7	3.58E–7
Effective Diffusion	5.5E–6	6.8E–6	4.1E–6	2.7E–6
TRO in Solvent Diffusion	6.2E–6	9.76E–6	6.67E–6	6.94E–6

TRO =

Examination of Table 5-2 shows how all four of the solvent-TRO binary pairs fit within the range of the infinite dilution coefficients derived by use of the Wilke-Chang equation. Given the inherent

inaccuracies caused by the estimated properties of TRO, the results provide strong evidence that the analytical solution is a legitimate method of calculating effective diffusion coefficients. As seen when applying the analytical solution to a new geometric configuration, such as the aluminum canister, the effective diffusion coefficients calculated are smaller but are within an order of magnitude (see Table 5-3).

Table 5-3. Comparison of the effective diffusion coefficients of the petri dish and canister

Solvent in Texaco Regal Oil	Effective Diffusion Coefficient (cm^2/second) Petri Dish	Effective Diffusion Coefficient (cm^2/second) Aluminum Can
Carbon tetrachloride	5.5E–6	3.05E–6
1,1,1-trichloroethane	6.8E–6	5.05E–6
Trichloroethene	4.1E–6	3.50E–6
Tetrachloroethene	2.7E–6	2.85E–6

Comparison of the effective diffusion coefficients for the binary and ternary shows a small decrease in the rates of diffusion for the four chlorinated solvents in the ternary system. This observation falls in line with the results of the thermodynamic analysis that suggests that the solvents will diffuse independent of any chemical interaction. The decrease in effective diffusion between the binary and ternary systems can be attributed to several factors that include:

- The decrease in the mole fraction of each component in the multicomponent mix will reduce the amount of solvent diffusing through the mixture

- Competition for pathways through the liquid matrix to the surface

- Decrease in the surface area at the liquid-gas interface during evaporation

All of these factors are attributed to the reduction in concentration of each solvent.

5.2   Conclusions

Thermodynamic analysis strongly suggests that the liquid fraction of Series 743 sludge is essentially an ideal mixture. Therefore, diffusion of each chlorinated solvent through the sludge matrix is independent of chemical interactions from the other liquid components of the mixture. Based upon this conclusion, no significant changes should be seen in the values of effective diffusion between the binary and ternary mixtures as they will diffuse independently.

The empirical approach using the modified Darken and Vignes equations was demonstrated to be an effective method of predicting effective diffusion coefficients. The resulting values of effective diffusion generated by the mathematical approach are within the same order of magnitude of the results of the analytical solution. One advantage to using the mathematical approach to estimate effective diffusion coefficients is that laboratory work is not required to get results.

Application of the analytical solution to experimental data produced values of effective diffusion that fall into the range of diffusion as predicted by the Wilke-Chang equation (infinitely dilute diffusion coefficients). Application of the analytical method to the ternary mixture reveals little change in the values of effective diffusion coefficients from the binary values. Comparison of the relative rates of

diffusion between the binary and ternary values demonstrates that there is little or no interaction between the solvents during diffusion.

Analysis of the mathematical equations suggests that, even in noninteracting mixtures ($\Gamma = 1$), the values of effective diffusion will change with different starting concentration. It is important to remember that effective diffusion coefficients are an average over a specific concentration (mole fraction) range. Therefore, reduction of the effective diffusion coefficients in the ternary mixture compared to the binary mixtures can be accounted for by the reduction of concentration of each solvent in the ternary mixture.

The results of this study suggest that both the analytical and mathematical methods are valuable tools for estimating effective diffusion coefficients. The mathematical methods of Darken and Vignes predict effective diffusion coefficients within the same order of magnitude of the analytical method. It has been documented that it is difficult to accurately determine concentration-dependent diffusion coefficients within an order of magnitude (Taylor and Krishna 1993). Considering the close proximity of all values of effective diffusion generated in this study, either method can be confidently used in estimating the diffusion of each chlorinated solvent out of the liquid fraction of Series 743 sludge.

The effective diffusion coefficient, although considered to be an average diffusion coefficient, has been shown to be an effective method of estimating mass transport through a defined bounded system. Although the analytical solution for transient diffusion did not match completely with the diffusion results obtained from canisters, it is assumed that there is an additional factor (head space) that affects diffusion characteristics. This factor introduces a condition that is beyond the physical parameters accounted for by the analytical solution of transient diffusion.

Introducing a solid matrix, such as calcium silicate to the solvent-TRO mixture, facilitates quicker solvent diffusion than what was observed in TRO alone, except for PCE, where the matrix seems to slow down diffusion relative to diffusion through TRO. These results may be explained through further investigation into the stereochemistry of interaction between the solvents and the solid matrix.

The presence of an escape hole in the canister, simulating drum corrosion, shows how the size of hole influences the rate of solvent escape from the drum. As the hole doubles in size, the rate of solvent escape also doubles. Considering other factors affecting solvent escape, Liekhus and Peterson (1995) identified VOC escape through polymer bagging. From this information, the time for a significant amount of VOCs diffusing through polyethylene bagging could be a matter of decades and not centuries. Not considered in this report are drum corrosion characteristics and solvent transport through soil, both of which would provide valuable insight for making appropriate predictions for solvent escape at the SDA.

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